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Cameron Engineers, Inc, Denver, Colo

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June 1977

EVALUATION OF BACKGROUND DATA RELATING TO NEW SOURCE PERFORMANCE STANDARDS FOR LURGI GASIFICATION

by

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**Contract No. 68-02-2152, Task No. 11
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ABSTRACT

This report contains information on expected emissions from a large coal gasification complex based on Lurgi technology. Use of best available control technology was assumed and two different schemes for sulfur removal were examined. The coal gasification plant was divided into 15 sections, with each section discussed in a separate chapter. Areas were identified in which projected emissions data were deemed inadequate for evaluating environmental impact. No major data gaps or inconsistencies were found, but more and better information is needed concerning effluents resulting from the venting of pressurization gas from the coal feed lock hoppers. This part of the plant is a potential source for emitting significant quantities of pollutants, particularly carbon monoxide. A summary of desirable information presently lacking in other areas is discussed also.

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1. INTRODUCTION

1.1 SCOPE OF EFFORT

This document is a first generation standards of practice manual. Due to the interest in the subject matter, this report is being published in its present form. The technical scope of information that will be addressed in future standards of practice manuals will be expanded. It is the objective of future manuals to provide all environmental requirements for a given plant type in one report.

The report is the result of a task group effort to review the state of the art for emission controls in first generation coal gasification plants. The objective of this effort was to provide to the Environmental Protection Agency a compilation of technical background information for use in assessing the need and level of Raw Source Performance Standards for coal gasification plants. Organizations involved in this task and the principal contact for each included Cameron Engineers, Inc. (J. E. Siner), Catalytic, Inc. (J. Cicalese), Hittman Associates (D. B. Emerson), and Radian Corporation (W. C. Thomas). The analytical technique used was to take published flow sheets for a particular plant and assign the various sections to different groups who would attempt to define all internal stream flows and effluents. Following the completion of the analysis of one particular plant design, it was anticipated that the next step would be to examine the effect of variations in coal feed, geographical location and process technology. This report covers only the first phase work -- analysis of a specific process and coal feed.

Major goals were the identification and characterization of all effluent streams. Where such information was not available from published design estimates, an attempt was made to provide "best guess" approximations. The time and funding available did not allow for rigorous design calculations. The scope of the analysis was specifically limited to the use of Lurgi gasifiers. Since there are no operating Lurgi installations in the U.S.A., information on detailed operating procedures is often sketchy and incomplete. Where operating procedures could affect the generation of effluents, it was necessary either to use engineering judgment in assuming a particular mode of operation or to consider more than one alternative procedure.

1.2 PROCESS SELECTION AND DEFINITION

The process design selected for analysis is that presented in "Second Supplement to Application of El Paso Natural Gas Company for a Certificate of Public Convenience and Necessity, Docket No. CP73-131, October 1, 1973". This was judged the most complete single source of publicly available design information for a coal gasification plant. Daily output of this plant is 288,600,000 standard cubic feet of synthetic pipeline gas with a heating value of 964 BTU/SCF. The coal feed is a low-sulfur subbituminous coal. The coal mining operation is not considered to be a part of the gasification plant. Heating value of the input coal is assumed to be 489.5×10^9 BTU/day.

Fuel for power and steam generation within the plant is obtained by gasifying coal in a set of air blown Lurgi gasifiers to produce a low-BTU fuel gas. This fuel gas is desulfurized before combustion. Overall plant balances for this design will thus be appreciably different than for a case where coal or tar is burned directly for on-site power generation.

The basic acid gas cleanup system considered is the Lurgi-licensed Rectisol process, as used in the El Paso design. Two different acid gas cleanup schemes are considered. Case 1-A uses Rectisol I with sulfur recovery via the Stretford process. Case 1-B considers the use of Rectisol II combined with a Stretford and a Claus unit for sulfur recovery followed by tail gas treatment.

2. EXECUTIVE SUMMARY

2.1 PROCESS SUMMARY

Estimated effluents from coal gasification plants have been published in a number of places, including environmental impact statements, FPC applications and various EPA reports. This report is a detailed review of emissions for one particular plant design -- the El Paso Burnham complex. Figure 2-1 is a summary of input, product and effluent streams for the complete plant. Each effluent stream is numbered and the same number key is used in Figure 2-2. Figure 2-3 shows the source for each stream in terms of the section of the plant involved and the chapter in this report which describes that section.

Table 2-1 presents a summary of all major streams recognized in this analysis. Air emissions are listed in Table 2-2. These values should be considered by plant designers as representative of achievable effluent levels for steady-state operation. Practical operating considerations for a plant of the size and complexity being studied will dictate that regulatory performance standards must allow some leeway for plant upsets, feed variations and general performance variations.

While the plant has been designed with extensive pollution controls, a number of streams must still be discharged to the environment. The magnitudes and characteristics of these streams are discussed in the following sections.

2.2 ENVIRONMENTAL CONCERNS

2.2.1. Air Emissions

Based on currently available data, the major streams contributing to air pollution appear to have been reasonably analyzed in previous efforts. No major data gaps or inconsistencies were discovered in the number presented in the El Paso FPC application, although the discussion of coal lock vent gases was incomplete and inadequate. The major pollutants discharged to the environment from the gasifier section consist of vent gases from the coal lock hopper,

AIR STREAMS

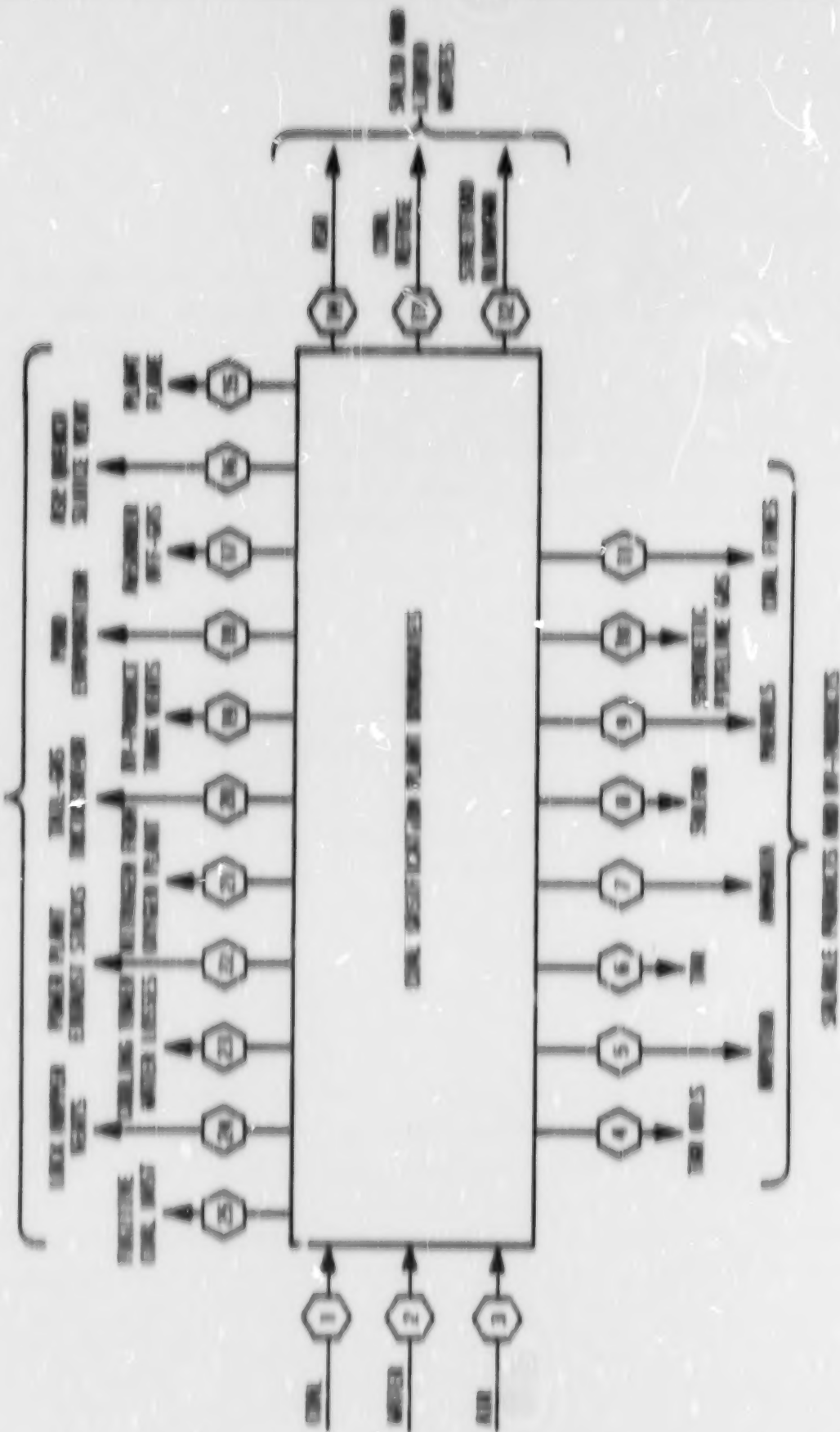
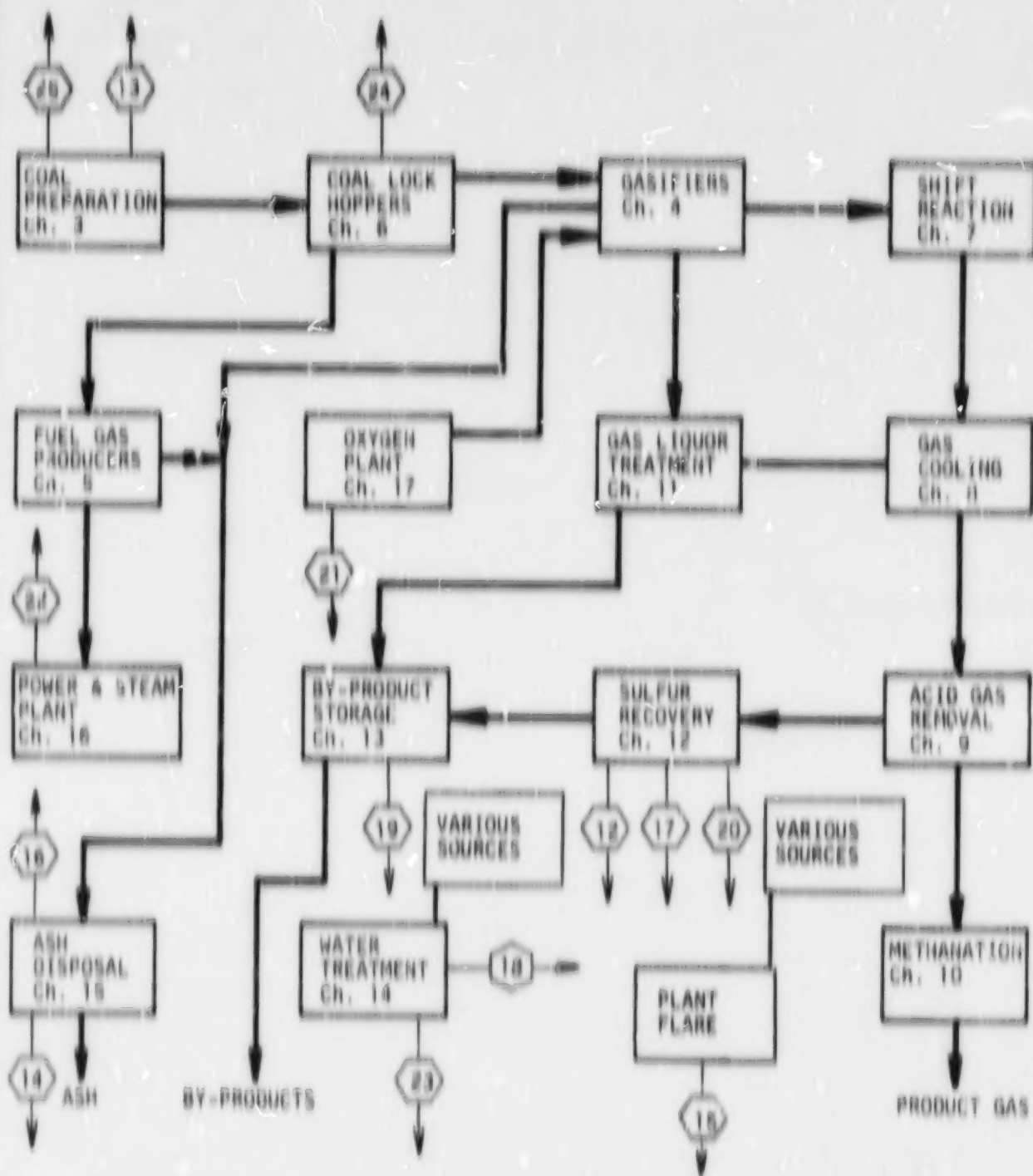


Figure 2-1. OIL DISTILLATION PLANT INPUT-OUTPUT STREAMS



Note: Ch. = Chapter Number

FIGURE 2-2. BLOCK FLOW DIAGRAM WITH EFFLUENT STREAMS

TABLE 2-1. STREAM FLOWS FOR FIGURES 2-1 AND 2-2

<u>Stream Number</u>	<u>Total Flow lbs/hr</u>
INPUTS:	
1. Coal	2,706,000
2. Water	3,660,000
3. Air	2,593,968
PRODUCTS & BY-PRODUCTS:	
4. Tar Oils	24,688
5. Naphtha	20,065
6. Tar	88,824
7. Ammonia	21,422
8. Sulfur	16,582
9. Phenols	11,271
10. SHG	813,760
11. Coal Fines	211,960
EFFLUENTS & WASTES:	
12. Stretford	Unknown
13. Coal Refuse	139,973
14. Ash	476,000
15. Flare	Unknown
16. Sluice Vent	Unknown
17. Off-Gas	1,803,872
18. Evaporation	80,210
19. Tank Vents	12.5
20. Incinerator	78,278
21. Nitrogen	1,587,462
22. Exhaust Stack	6,483,000
23. Cooling Loss	1,483,000
24. Hopper Vent	2,673
25. Fugitive Dust	121

The lock hoppers are pressurized with cooled raw product gas. After reaching system pressure, coal is fed into the gasifier. When the coal lock hopper is empty, the pressurizing gas is vented to a lock gas holding vessel which operates near, but slightly above, atmospheric pressure. As the fresh charge of coal is dumped into the hopper, it displaces to the atmosphere the residual gases remaining in the hopper.

Estimates made in this study show that the gas vent rate is about 8,573 lb/hr. and contains H_2S , CO_2 , CH_4 , CO , non-methane and non-ethane hydrocarbons, and coal dust. A number of different gas compositions could be vented and varying amounts of individual constituents would be discharged depending on the source of the gas used. If the gas were not recycled at all but completely vented, the total discharge would be on the order of 82,000 lb/hr. Worst-case emission, relative to coal feed rate, would be as follows:

<u>Components</u>	<u>Potential Emissions lbs/10⁶ BTU Coal</u>
H_2S	0.022
CO	1.0398
CH_4	0.310
NMH	0.083

Carbon monoxide emissions from uncontrolled venting could be a major problem. Because of the economic value of the pressurizing gas, however, it would undoubtedly be recycled to the maximum extent possible. Further control, if needed, could be accomplished by the use of exhaust fans and incineration.

Atmospheric discharge streams from the sulfur recovery section include vent streams from the lean H_2S absorber and oxidizer (stream #17), and stack gas from the H_2S incinerator (#20). The vent stream from the absorber and oxidizer contains appreciable quantities of CO_2 (67 ppmv), some H_2S and traces of CS_2 . Total hydrocarbons including CH_4 and C_2H_6 are 9,400 ppmv and CO emissions are 1600 ppmv. The high levels of hydrocarbons, CO , and CO_2 released are a major source of concern and various control methods should be studied.

At present, the only proven method for treatment would be the incineration of organic sulfur compounds and hydrocarbons. It should be noted that the emission levels are based on study group estimates. Exact emissions from an operating plant could vary considerably.

The incinerator stack gas (#20) consists of CO_2 , H_2O , SO_2 , and NO_x . The estimated SO_2 and NO_x levels are 350 ppmv and 70 ppmv, respectively. These gases may require desulfurization because of the relatively high SO_2 content. Various venturi scrubbers/packed column systems are available for gas treating.

The by-product storage area will also represent a pollution source for the complex. Discharges (#19) will result from tank breathing, leaks, spills and venting of tanks during filling. Estimated emission rates for the tank farm are as follows:

• Crude phenol	• 1.5 lbs/hr.
• Tar Oil	• 2.6
• Naptha	• 2.1
• Ammonia	• 1.6
• Product gases	• 3.2
• Methanol	• 1.6

Control of vapor emissions could be achieved by a vent condenser which circulates refrigerated brine at 0°F or by scrubbing the vent vapors with a low volatility solvent.

Evaporation from the waste pond (#18) and misting and evaporation losses from the cooling towers (#23) add about 1,563,210 lbs/hr. of water vapor plus traces of organic compounds, and non-methane, non-ethane hydrocarbons to the atmosphere. Although only trace amounts of these contaminants are expected, no hard data exists on the exact quantities. Further studies are needed to determine the amounts emitted and effects on the immediate environment.

Discharge of the hot gasifier ash in the ash transfer sluice, produces a small but totally unfiltered stream to the atmosphere. The hot ash is quenched with contaminated process water and produces varying amounts of steam. This steam contains ash particles and possibly traces of organic compounds which could be formed from contacting the waste water (which has a high organics content) with hot ash containing unreacted carbon. The nature and quantity of these compounds is unknown, as well as the amount of steam produced. It is not expected that this discharge would present a hazard, but more information should be obtained to confirm that it does not.

By far the largest single discharge from the complex is the stack gases generated by combustion in the steam and power generation section of the plant. The total stream flow rate (#22) is approximately 8,960,390 lbs/hr. of combustion products such as SO_2 , NO_x , H_2O , CO_2 , CO, hydrocarbons and air. Since the fuel to the combustion operations is treated fuel gas, the stack gases contain negligible amounts of particulate matter. Use of excess air during combustion will minimize the amount of CO and hydrocarbons in the gas. The total effluent from the stacks meets current air pollution standards and therefore is discharged directly to the atmosphere.

Emissions from the coal handling and preparation area consists of fugitive dust (stream #25) produced by the crushing, screening, conveying, stockpiling, reclaiming, and coal fines cleaning operations. The control method proposed by El Paso would use water sprays with a wetting agent installed at transfer points, truck dump hoppers, etc. It is estimated that the total fugitive dust emissions would not exceed 121 lbs/hr. The control method chosen is an effective proven method and the emissions listed are probably the minimum achievable level without the addition of other equipment such as exhaust fans and hoods.

Although carbon dioxide emissions are usually considered to be inert, the large amounts emitted from a commercial gasification facility call for a careful evaluation of local effects. Although similar in quantity to that emitted at a large power plant, the effect of lower stack temperatures should be studied carefully in dispersion models.

A summary of air emissions is given in table 2-2.

2.2.2 Water Effluents

The geographical location of the El Paso complex makes it possible to design for zero discharge of water effluents. In other parts of the country, where it is not possible to dispose of contaminated water by solar evaporation, water pollution may be a major concern.

The contaminated water discharge to the evaporation pond is not considered an effluent since none of the water is returned to the San Juan River. However, two potential escape routes for the water from the holding pond exist. One route would be an accidental breaching of the pond dikes. In this case, contaminant control measures would be immediately enforced and damage to the area minimized. The second route, which is potentially more troublesome, involves the possibility of permeation of contaminated water through the pond bottom. This migration could expose groundwater in the area to all the components in the pond water, and create an extreme pollution problem. Extraordinary care should be used in construction of the pond and monitoring of possible waste water migration.

In some areas the coal seam being mined constitutes a part of a groundwater aquifer. Leaching of ash and other plant wastes which have been returned to the mine for disposal can then result in a deterioration of groundwater quality. Although such concerns are outside the scope of this study, much more attention should be devoted to ash leachability in areas with significant groundwater flow.

2.2.3 Solid Waste Disposal

Coal refuse from preparation and handling, and ash from the gasifiers are the two major solid discharge streams. The coal refuse from the preparation section is trucked back to the mine site for disposal. This is an effective method of control and disposal for this material. The ash from both the oxygen and air blown gasifiers is transported to ash handling with contaminated process water. The ash slurry undergoes classification and dewatering. The coarse, dewatered ash is transferred to the mine for disposal. Fine ash

from the classification step and the main water stream are sent to a thickener. The underflow containing the ash fines are sent to a fine ash settling pond. The settled fines in the pond are periodically removed and sent to the mine site for disposal. While the ash itself is well contained by burial, a number of constituents in the ash could become a pollution hazard if leaching were to occur. An uncertain amount of trace elements are concentrated in the ash and various organics from the quench water are also present. As pointed out in the discussion of water effluents, the possibility of water pollution due to leaching from the solid wastes is highly dependent on local climate, rainfall and groundwater conditions. A thorough analysis of all these factors is required for each plant site in order to determine the best procedure for solids disposal.

2.2.4 Occupational Health Issues

Health statistics on occupational groups in other coal conversion operations, such as coke ovens and coal tar processing, have shown significantly higher lung cancer rates than groups without such occupational exposure. Several other diseases and types of cancer may be found to have higher incidences also. Although no comparison should be made between coke ovens, where worker exposures are extremely high, and gasification plants where process streams are almost totally controlled, the fact that the same types of materials will be present indicates that occupational health concerns must be addressed carefully and thoroughly. No data were discovered in this study to suggest a significant health problem with the proposed plant design.

2.2.5 Trace Metals

Because of the large quantities of raw materials consumed, on the order of 20,000 to 30,000 tons of coal per day, there is a potential for discharge of large quantities of material which may be present only in very low concentrations. Neither the fate nor the effects of trace elements are clearly understood, but many are either toxic or carcinogenic and others may act as

mutagens or teratogens.

Nickel, arsenic, cadmium and lead are among the hazardous metals whose flow rate through the plant can be as high as several pounds per hour. If released to the environment in sufficient quantity these materials could lead to undesirable environmental effects.

2.2.6 Polycyclic Aromatic Hydrocarbons

Many of the by-product streams will have high concentrations of polycyclic aromatic hydrocarbon compounds. The concentrations will be much higher than in comparable petroleum derived liquids. As a general class, many of these compounds are known or suspected carcinogens. Eventual use of the by-products by consumers, or ultimate disposal of manufactured products should be investigated to be sure that environmental contamination by PAH's does not occur. Within the gasification plant itself, workers must be protected from exposure, even to relatively low levels of PAH in the atmosphere.

This analysis did not reveal any obvious route for substantial quantities of PAH to be released. One possible source could be the vent gas from the coal lock hoppers. It is recommended that such gases be controlled and collected locally by hoods and exhaust fans as necessary.

2.2.7 Secondary Pollution Effects

Secondary effects are defined as those which result off-site from the use of plant products, by-products or waste streams. In order to assess the overall environmental impact from a gasification complex, any such secondary pollution should be identified.

The product gas will be pipeline quality; that is, it will satisfy various standards set up by the government and the natural gas industry. It will be distributed in the existing natural gas pipeline system for residential, commercial and industrial usage. The composition of the final SNG product stream is estimated to be as follows:

Component	Volume %	Flow Rate, lbs/hr
CH ₄	92.92	473,512
H ₂	4.19	2,661
CO ₂	1.81	26,310
N ₂ + Ar	1.08	12,106
CO	0.010	122
Other HC's	0.0116	

No information developed in this analysis would indicate that burning SHG will result in any new or different pollution than burning natural gas. Certainly the use of SHG will result in much less sulfur pollution at the point of final consumption than would the use of an equivalent amount of coal or oil at the same point. As nearly as can be determined, all volatile trace metals and heavy polycyclic hydrocarbons should be removed from the product streams. However, this assumption should be verified carefully in an operating plant to be sure that trace metals or compounds such as carbonyls do not appear in the product by unforeseen mechanisms.

Useful by-products from the gasification plant include tars, tar oils, naphtha, ammonia, sulfur and phenols. The tars, tar oils, naphtha and phenols could be burned directly as fuel or used as raw materials for a large variety of chemical products. If used directly as fuel, the sulfur and trace metal contents may be of concern. The sulfur content of the tar is estimated to be 0.77% and of the tar oil 0.29%. In general, in order to meet sulfur emissions limitations, a high sulfur fuel oil will be blended with a low sulfur oil until an acceptable sulfur level results. The same technique could be applied to combustion of the tars.

Due to the large pitch or residue content of the tar, excessive soot may be formed in some equipment. These particulates would then be discharged with the stack gases.

Many of the trace elements found in coal may be found in the tar. Some of these include antimony, arsenic, boron, bromine, cadmium, fluorine, lead, mercury and nickel. During combustion, some of these elements may be released

to the atmosphere in various forms. Data are lacking with respect to both the quantities of various elements and the actual compounds formed.

Acceptable technology for control of sulfur emissions are available including desulfurization of the fuel, blending with low-sulfur fuels, stack gas scrubbing, etc. Sulfur in coal tars can be controlled by any of these methods, so no new problems are likely to occur. Control and removal of trace elements may be a much more difficult problem. When coal is burned directly, most of the trace elements are recovered in either the bottom ash or the fly ash. Extensive research has shown, however, that many trace elements are released and their buildup in areas downwind from the plant can be carefully analyzed. The concentration of any trace elements in the tar, along with the lower ash content and different burning characteristics of tar could result in an entirely different spectrum of emissions from a tar-burning boiler. More studies are needed in this area.

Recycle of tar back to the gasifier is a direct method of control which has been proved in operation.

Tar oils, as with tar can be burned directly or refined. An advantage of tar oil is that it is a much lighter stock and more easily refined.

The naphtha produced in the plant appears to be much like its conventional petroleum counterpart. Some may be used as a cutter stock to reduce the viscosity of the tar before it is used in boiler furnaces. The trace element concentrations in naphtha should be minimal, and secondary pollution from naphtha should be basically the same as from the use of petroleum naphthas.

Ammonia and sulfur streams should be no different than those produced by other processes.

Possible by-product uses other than fuels are listed below, along with the current major source for each. Although the gasification by-products will more nearly resemble coke oven products than petroleum, there are appreciable differences even here. Gasification tar and tar oil contains relatively high proportions of solids, water, acids and nitrogen. If the

Product	Current Dominant Source	
	Petroleum	Coke Oven
Benzene	X	
BTX crudes	X	
Phenol (natural/refined)	X	
Cresylic acids	X	
Naphthalene		X
Cresote		X
Carbon black feedstock	X	
Electrode pitch		X
Delayed coke	X	
Fluid coke	X	
Specialty tar coatings, pitches, enamels		X
Road tars	X	
Distillate/residual fuel stocks	X	
Gasoline pool stocks	X	

gasification by-products are used to displace petroleum-derived products, then the much higher content of polycyclic aromatic hydrocarbons may become a matter of concern.

Without knowing in advance what the actual disposition of the by-products will be, it is impossible to form even qualitative estimates of secondary pollution impacts.

2.3 NEW TECHNOLOGY NEEDS

This study suggests that there are two major areas in which new or improved technology is desirable in order to improve either the efficiency or the economics of pollution control. The first area is removal of organic (mostly COS) sulfur from the gas stream. Although sulfur as COS is only a small percent of the total sulfur contained in the crude gas, by the time conventional sulfur removal techniques have been applied, COS may be the major sulfur constituent. Thus a further reduction in sulfur emitted is possible only by attacking COS.

The second area for improvement is a better technique for control of hydrocarbon emissions than incineration. In some cases a stream requiring incineration can simply be added to a boiler furnace so that little additional fuel is used. In other cases the stream may be so large that this would not be practical.

2.4 PROCESS DATA NEEDS

One of the most troublesome aspects of operating pollution control equipment in coal conversion plants is likely to be the variability of the feed coal. Coal is not a uniform substance and its chemical properties may change markedly over short distances in the deposit. These changes can cause fluctuations in the compositions of all process streams, with resulting fluctuations in the performance of pollution control equipment. The information upon which this report was based consists mostly of design data from various proposed coal gasification projects. These data are really feasibility studies based on laboratory analysis of coal core samples and engineering estimates for the composition of process streams. Although the accuracy of the assumptions which went into the engineering estimates will probably not be critical with respect to the overall operation of the coal gasification plants, it could have a very large effect on sulfur emissions and on the efficiency and operability of emission control devices.

Tests results in a Lurgi gasifier with American coals exhibit a wide range of sulfur concentrations in the raw gas due to variability of the feed. Variations in the coal produced from any one mine will depend on whether a single or multiple seams are being mined as well as individual deviations within a seam. A critical parameter is the amount of sulfur appearing as COS, because of the difficulty of removing COS. According to testimony presented to the National Air Pollution Control Techniques Advisory Panel, COS concentrations may be twice as high as that predicted by Lurgi for a given ratio of organic to pyritic sulfur in the coal.

Actual operating data, in terms of concentrations as a function of time, rather than grab sample results, are urgently needed. Without information of this type it is impossible to say whether certain sulfur removal systems would be effective. Trace metal balances are needed. Although some liquid and solid trace metal analyses have been conducted, meaningful material balances for individual elements could not in general be closed with satisfactory accuracy. As a result, information available to date is only qualitative at best.

The composition of gases vented during ash quenching is completely unknown.

The following types of data are the most urgently needed:

1. The time variation of effluent production under normal "steady state" operations.
2. COS concentrations as a function of definable coal properties.
3. Closed material balances for important trace elements.
4. The influence of operating parameters and fluctuations on crude product properties.

2.5 RESEARCH DATA NEEDS

The foregoing section discussed data which can only be obtained from a large operating plant. However, there are many areas in which improved knowledge of pollution parameters can be obtained by research conducted at a smaller scale. For instance, pilot plant results for the CO₂ Acceptor process have shown essentially zero generation of heavier hydrocarbons in the raw gas. There is presently no satisfactory explanation for this phenomenon, but if process conditions can be adjusted to reduce the output of such materials the effect on pollution control costs could be substantial.

Much additional information on trace element distributions is needed, including not only their location in various by-product and process streams but also their form (reactivity, solubility, leachability, etc.). Not all forms of trace elements are toxic; it is important to know which compounds are hazardous and which compounds are formed and/or emitted during gasification. For instance, nickel carbonyl was detected in the product during operation of a Lurgi gasifier at Westfield, Scotland a number of years ago. This highly toxic material is known to be carcinogenic in the respiratory system and its presence in any vent streams could be an occupational hazard.

3. COAL HANDLING AND PREPARATION

3.1 STREAM FLOWS

Figure 3-1 is a schematic flow diagram of the coal handling and preparation facilities. These facilities produce two sizes of coal feed for the plant (44.45 mm x 2mm and 8mm x 2mm) plus coal fines (less than 2mm) for sale.

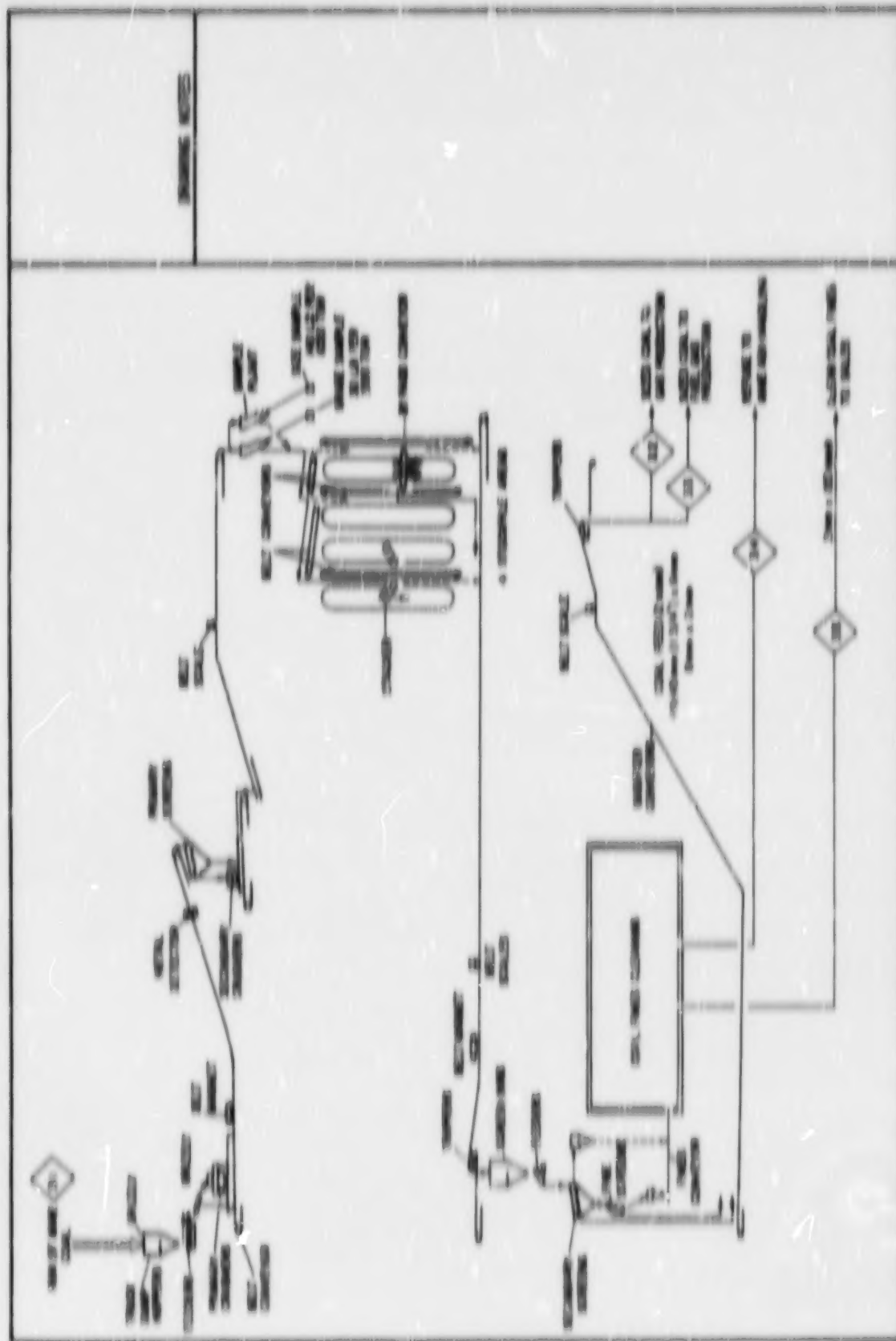
Run-of-mine (ROM) coal will be received from the mine by trucks and dumped into hoppers with a 36" grizzly on top. The 36" x 0 coal will be fed over a 6" grizzly and the 36" x 6" oversize crushed to minus 6". The 6" x 0 coal will be primary screened at 1-3/4"(44.45 mm) and the oversize secondary crushed to minus 1-3/4". The primary and secondary crushers are designed to operate ten shifts per week at 3,614 TPH.

The coal sampling and stockpiling equipment are designed to operate 10 shifts per week at 3614 TPH and the reclaiming, screening and fines cleaning equipment are designed to operate 7 days per week, 24 hours per day at 1800 TPH. Approximate inventory in the four stockpiles is 12 days plant feed (about 350,000 tons).

Table 3-1 lists stream flows for these facilities and Tables 3-2 and 3-3 are the components and trace element analyses of the coal. Stream compositions for the product from coal fines cleaning and the refuse from the coal fines cleaning plant were estimated on the basis of 95% of the ash being contained in the refuse stream.

Table 3-1. STREAM FLOWS OF COAL RECEIVING AND HANDLING FACILITIES
(POUNDS PER HOUR, AVERAGE)

Stream	<u>3.1</u>	<u>3.2</u>	<u>3.3</u>	<u>3.4</u>	<u>3.5</u>
Coal	1,746,370	1,250,310	268,063	52,868	174,129
Ash	620,906	373,220	80,012	64,359	3,388
Water	<u>439,725</u>	<u>314,950</u>	<u>67,522</u>	<u>22,746</u>	<u>34,443</u>
Total	2,706,000	1,938,480	415,597	139,973	211,960



THE RESULTS

Table 3-2. COMPONENT ANALYSIS OF COAL (MAF)

	<u>Weight %</u>
Carbon	76.26
Hydrogen	5.58
Nitrogen	1.32
Sulfur	1.07
Oxygen	15.74
Trace Compounds	<u>.03</u>
	100.00

Table 3-3. TRACE ELEMENT CONCENTRATION IN COAL⁽³⁾

<u>Element</u>	<u>Concentration in p.p.m. by weight</u>	
	<u>From</u>	<u>To</u>
Antimony	0.3	1.2
Arsenic	.1	3.0
Bismuth	.0	.2
Boron	60.0	150.0
Bromine	.4	18.0
Cadmium	.2	.4
Fluorine	200	780
Gallium	.5	8.0
Germanium	.1	.5
Lead	1.4	4.0
Mercury	.2	.3
Nickel	3.0	30.0
Selenium	.1	.2
Zinc	1.1	27.0

3.2 POTENTIAL EFFLUENTS

3.2.1 Major Effluents

The major effluent from these facilities is expected to be particulates produced by the crushing, screening, conveying, stockpiling, reclaiming and coal fines cleaning operations. Water runoff from the area also may be contaminated with suspended coal particles or compounds leached from the storage pile. Some methane may be evolved from the coal while in storage, as indicated by SASOL⁽⁴⁾.

The El Paso FPC application does not characterize these effluents or estimate their discharge rates. WESCO indicated that only trace amounts of particulates are expected from the coal handling facilities⁽²⁾. Wyoming Coal Gas Company estimated particulate emissions of 0.06 pounds per ton of coal for the crushing, screening and conveying operations⁽¹⁾. Wyoming Coal Gas Company also estimated particulate emissions of 0.025 to 0.04 pounds per ton of coal handled for the coal storage and reclaiming facilities. Utilizing these estimates for the El Paso design results in an estimated 101 to 121 pounds per hour of uncontrolled particulates emitted from the coal handling and preparation facilities.

The amount of runoff will be highly variable and depend primarily on local climatic conditions and extent of enclosures for the coal storage area. No estimate of methane evolved from the coal during storage is available.

3.2.2 Trace Constituents

Trace constituents emitted from these facilities would be those contained in the coal particulates produced by the crushing, screening and conveying operations. Table 3-2 is a trace element analysis of the coal.

3.3 CONTROL METHODS

The planned pollution control methods for these facilities as stated in the El Paso FPC application are: water sprays with a wetting agent will be used at all transfer points, truck dump hoppers, crushers and screens; and dust collectors will be installed in the screening plant. Water use for dust suppression was

estimated at 20 gpm per transfer point. Total water use for the estimated 17 transfer points is 340 gpm. This water is supplied by the water stream indicated for mine use. The physical preparation facilities are not described in enough detail to suggest other specific controls. Some potential methods to minimize or control pollutants include:

- enclosing screening and coal fines cleaning operations and controlling particulates by use of wet scrubbers or baghouses.
- collecting and treating runoff from the storage piles.
- preventing spontaneous combustion in storage piles by avoiding segregation of fines and compaction.
- covering conveyors.
- using a baghouse filter to treat air exhausted from the sampling facilities.
- controlling the height of the stacker such that the free fall of the coal onto the pile is minimized thus reducing the coal dust emissions produced during the stacking operations.

3.4 PROCESS MODIFICATION

None suggested.

REFERENCES

1. Wyoming Coal Gas Company, "Applicants Environmental Assessment For A Proposed Gasification Project In Campbell And Converse Counties, Wyoming", October, 1974.
2. WESCO, "Final Environmental Statement - Western Gasification Company, Coal Gasification Project And Expansion of Navajo Mine by Utah International Inc.", January 1976.
3. El Paso "Draft Environmental Statement - El Paso Coal Gasification Project", July 1974.
4. Communication with EPA.

4. GASIFICATION

4.1 STREAM FLOWS

The gas production section of the plant consists of 28 oxygen blown Lurgi gasifiers operating at 435 psig. Initial plans call for the use of 24 gasifiers for actual production with 4 gasifiers as standbys. These units will produce 288 MMSCFD of synthetic crude gas from 23,261 tons of coal feed. The process flow for this section of the plant is illustrated in Figure 4-1.

Streams to the gasifier consist of coal, steam and oxygen. Initially, sized coal from coal preparation is fed into the coal bunker atop the gasifier (see Figure 6-3). The coal is then dropped into the coal lock which is subsequently pressurized and opened to the gasifier. The coal then flows down through the gasifier where crude gas, tar, tar oil, naphtha, phenols and other compounds are formed. This crude gas exits the gasifier for cooling, separation, and further processing. The remaining material, ash and some unreacted coal, are dumped out of the bottom of the gasifier to a lock and ash quench system. The quenched material is then transported via a sluiceway to an ash handling area.

4.1.1 Coal Feed

The crushed and sized coal is fed to the gasifiers at the rate of 1,938,480 lb/hr. Component flow rates are given in Table 4-1.

The component analysis for the moisture and ash free coal is given in Table 4-2.

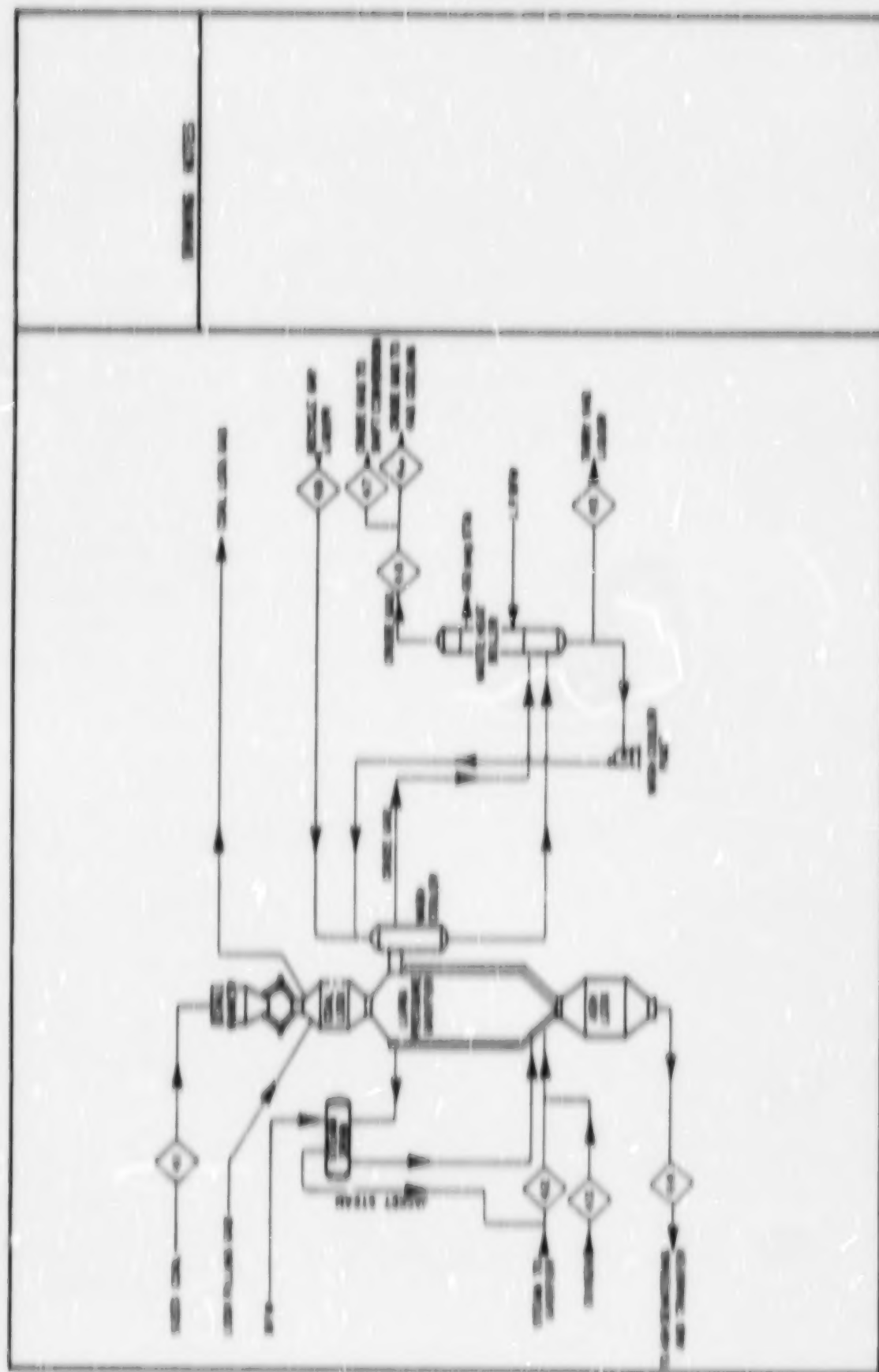


Figure 4-1. Flowchart for the study.

Table 4-1. MATERIAL BALANCE FOR GAS PRODUCTION

Stream Number Component	4.1 lbs/hr	4.2 lbs/hr	4.3 lbs/hr	4.4 lbs/hr	4.5 lbs/hr	4.6 lbs/hr	4.7 lbs/hr	4.8 lbs/hr
CH_4						1,333,502	729,157	604,345
H_2						13,538	7,425	6,115
C_2H_6						12,273	6,770	5,503
C_3H_8						671,677	334,864	337,273
H_2						84,849	46,401	38,448
C_2H_4						193,807	105,537	87,470
C_2H_2						19,730	10,700	8,942
$\text{H}_2 + \text{Ar}$			18,275			11,267	6,405	5,376
O_2			487,365			—	—	—
Total Dry Gas			478,640			2,380,447	1,385,965	1,033,502
Water	314,450	1,363,540			—	1,364,940	762,764	532,156
Coal (MBF)	1,358,300			79,629	—	—	—	—
Ash	373,200			573,270	—	—	—	—
Naphtena						28,065	10,939	9,086
Tar Oil					11,963	28,007	15,314	12,633
Tar					65,811	6,630	3,999	3,375
Crude Phenolics					173	8,272	4,901	4,136
H_2						15,978	9,640	7,989
TOTAL	1,958,400	1,363,540	478,640	302,829		3,757,469	2,054,592	1,705,697

Table 4-2. MOISTURE AND ASH FREE COAL ANALYSIS⁽¹⁾

<u>Component</u>	<u>WT %</u>	<u>Lb/Hr</u>
Carbon	76.26	1193,479
Hydrogen	5.58	89,767
Nitrogen	1.32	16,504
Sulfur	1.07	13,373
Oxygen	15.74	25,797
Trace Compounds	<u>0.03</u>	<u>375</u>
TOTAL	100.0%	1,250,300

Trace elements in the coal, while averaging only .03% of the total weight, represent a potential pollution problem. Because of this, their distribution in the gasifier system will be estimated in Section 4.1.6. Table 4-3 gives a range of trace element flow rates into the gasifier system based on the trace element concentrations listed in Table 3-3.

4.1.2 Steam and Oxygen

The sources of steam for the gasifier include the normal steam generation system as well as steam generated in the gasifier cooling water jacket. Water fed to these systems consists of treated and demineralized river water. It will be assumed that this is pure water and will not contain enough trace constituents to have an effect on the overall trace constituent balance. The combined steam rate is 1,783,540 lb/hr at 550 psig and 750°F. Oxygen is supplied to the gasifier at 510 psia. This stream consists of 460,365 lb/hr of oxygen with 10,275 lb/hr of $N_2 + Ar$. The oxygen is produced by standard air separation methods.

Table 4-3. TRACE ELEMENTS (POUNDS PER HOUR)

Element	From	To
Antimony	1.5	0.375
Arsenic	3.75	0.125
Bismuth	0.25	0.0
Boron	187.5	75.0
Bromine	22.5	0.6
Cadmium	0.50	0.25
Fluorine	975.0	250.0
Gallium	10.0	0.625
Germanium	.625	0.125
Lead	5.0	1.75
Mercury	0.375	0.25
Nickel	37.5	3.75
Selenium	0.25	0.125
Zinc	33.75	1.375

4.1.3 Crude Gas

Processing of the crude gas begins by passing the 650°F gas through a direct contact wash cooler immediately after the gasifier, to condense liquids and remove coal dust and ash. The gas is further cooled to 370°F in a waste heat boiler which produces 100 psig steam. During the cooling, various amounts of tar, tar oil and trace compounds are condensed and removed. Steam condensed from the crude gas in downstream processing is recycled back to the gasifier area for use as the cooling agent in the direct contact cooler. During this processing, the crude gas picks up approximately 92,000 lb/hr of water which it carries out of the area. Immediately following the waste heat boiler, the gas stream is split. Approximately 45% of the gas is sent to crude gas cooling while the remainder is sent to the water-gas shift unit for CO conversion. The composition and flow rate of the crude gas stream as it leaves the gas production area is given in Table 4-1.

4.1.4 Tarry Gas Liquor

Water condensed from the crude gas in the shift conversion and gas cooling areas plus recycle water from the gas liquor separation area

is sent back to the gas production area for use in the wash cooler. This water stream, along with the tar, tar oil and crude phenols condensed from the gases during cooling comprise the tarry gas liquor stream. Approximately 94.3% of the tar, 44% of the tar oil and 3.3% of the crude phenols produced in the gasifier are contained in this stream.

After leaving the gasifier area, the stream is subsequently processed for removal of the various by-product constituents. The flow rates of the major components of the stream (excluding trace elements) are given in Table 4-1. A total flow rate for water, which is the largest constituent, was not available.

Besides the major components, varying amounts of CO_2 , H_2S and HCN plus coal dust and ash will also be contained in these streams. No data was available to allow an estimate of these constituents.

The composition of the tar and tar oil from the gasifier for the El Paso case is not known. However, various operations at the Westfield test center in Westfield, Scotland using a Lurgi gasifier generated some data in this area. The exact composition of the tar and tar oil will change from coal to coal and is dependent on operating conditions. Two analyses are given in Tables 8-2 and 8-3, Chapter 8.

The expected sulfur content of the tar and tar oil for the El Paso design are as follows:

	<u>Wt. % Sulfur</u>	<u>Pounds per Hour Sulfur</u>
Tar	0.616	339.1
Tar Oil	0.99	118.7

4.1.5 Ash

Ash produced in the gasifier is discharged through the bottom of the gasifier via a revolving grate. This 500°F ash falls into a pressurized ash lock. The lock dumps approximately every 20 minutes into an ash quench system where a mixture of water streams from the plant are added. The wet ash and excess water are transferred in a sluiceway to wet ash dewatering and handling.

During the quenching process a large amount of steam containing ash dust and clinkers is produced. This mixture is first sent to a wet cyclone for removal of clinkers and then to a condenser for condensing the steam and removing fine ash particles. Along with the steam, some amount of non-condensable gases may be formed due to organic materials in the quench water and unreacted carbon in the ash. The quantity and composition of this gas stream is not known, but it will be discharged from the gasifier.

The major quenched ash components are listed in Table 4-4.

Table 4-4. QUENCHED ASH STREAM

<u>Component</u>	<u>Rate</u> <u>(Pounds per Hour)</u>
Water	422,950
Unreacted Coal	19,639
Ash	373,220
TOTAL	815,809

In order that individual components may be followed, a total stream analysis is given in Table 4-6.

Table 4-5. ASH STREAM COMPONENT ANALYSIS

<u>Unreacted Coal Analysis</u>	<u>Rate</u> <u>(Pounds per Hour)</u>
Carbon	14,976
Hydrogen	1,096
Nitrogen	259
Sulfur	210
Oxygen	3,091
<u>Dry Ash Analysis</u>	
SiO ₂	231,396
Al ₂ O ₃	93,405
Fe ₂ O ₃	18,662
CaO	14,656
MgO	3,359
K ₂ O	2,985
Na ₂ O	5,598
TiO ₂	3,359

A breakdown of the quench water streams is given in Table 4-6.

Table 4-6. ASH QUENCH WATER

<u>Source</u>	<u>Rate</u> <u>(Pounds Per Hour)</u>
Blowdown	110,338
C-T Blowdown	135,508
Contaminated gas liquor	135,508
Process condensate	413
Utility Water	41,183
TOTAL	422,950

4.1.6 Trace Elements

Trace elements in the gasification system represent only a small percentage of the total feed. However, during the year approximately 3.3 million pounds of these elements are introduced into and come out of the gasification plant. The distribution of these elements must be known so the environmental impact of their disposal can be accurately assessed and containment methods can be devised if necessary.

Unfortunately, few quantitative analyses have been made of the fate of these elements in gasification plants. Various attempts have been made to follow these materials through the system. A recent effort⁽⁶⁾ at the Pittsburgh Energy Research Center involved a trace element balance around the Synthene PDU. The results indicate a general pattern for distribution and also emphasize the problem of following these small quantities of materials. Percent recoveries ranged from 17.2% to 1,103.7%.

Other Studies⁽³⁾⁽⁴⁾ have also been conducted which were only qualitative in nature. The El Paso EIS does not address the trace element problem. However, WESCO did attempt to quantify distribution within their system. An existing NASA computer program was used to evaluate volatilities, kinetics and chemical interchange of the trace elements and 200 different oxides, sulfides, hydrides, fluorides and carbonates formed by the trace elements. The results of this effort are also qualitative in nature, but are shown in Table 4-7.

Table 4-7. TRACE ELEMENT DISPOSITION⁽²⁾

1800°F		650°F		45°F		-90°F	
Vapor	Condensed	Vapor	Condensed	Vapor	Condensed	Vapor	Condensed
Hg	Major Ash Components plus Be and As (estimate 4.9 ppm)	Hg	Pb (PbS)	Hg	Cd	Hg(8.6%)	Hg(91.4)
Sb		Sb	F	Te	Se		Te(6.7)
Se		Se		(6.7%)	Sb		
					Te(93.3%)		
Te		Te					
Cd		Cd					
Pb							
F							

The Sasol complex in South Africa is currently operating Lurgi gasifiers to produce town gas. Operating data on trace element distribution has been made available. Although the coal and operating conditions differ, this data can be used to estimate the distribution of elements for the El Paso complex. Comparing these estimates with results of the studies previously mentioned, indicate that all the results fall into a general pattern. Tables 4-8 through 4-11 are estimates of the trace element distributions in the gasifier area.

No breakdown was given for the crude gas. While there will be some trace elements in the gas, they will ultimately be collected in the tarry gas liquor stream.

Table 4-8. TRACE ELEMENT DISTRIBUTION - GASIFIER ASH

<u>Element</u>	<u>Maximum Rate (Lb/Hr)</u>
Antimony	0.75
Arsenic	1.01
Boron	172.50
Bromine	2.44
Cadmium	.26
Fluorine	546.0
Lead	4.68
Mercury	.191
Nickel	37.33
Zinc	33.75

Table 4-9. TRACE ELEMENTS - TARRY GAS LIQUOR (WATER)

<u>Element</u>	<u>Maximum Rate (Lb/Hr)</u>
Antimony	.875
Arsenic	2.49
Boron	12.18
Bromine	20.03
Cadmium	.225
Fluorine	428.19
Lead	.1027
Mercury	.1511
Nickel	.153

Table 4-10. TRACE ELEMENTS - TAR, TAR OIL
(Maximum Rates, Lbs/Hr)

Element	TAR DISTRIBUTION		TAR OIL DISTRIBUTION	
	Gas	Liquor	Gas	Liquor
Antimony	.0032	.053	.0106	.00836
Arsenic	.047	.079	.0892	.070
Boron	.159	2.64	.0042	.0033
Bromine	.0018	.029	--	--
Cadmium	.00026	.0042	.0058	.00462
Fluorine	.044	.736	.0164	.0128
Lead	.0123	.204	.00046	.00036
Mercury	.0017	.0287	.0014	.00107
Nickel	.00064	.0106	.0012	.0099

Table 4-11. TRACE ELEMENTS PERCENT BREAKDOWN
All Streams(6)

Element	Ash%	Tarry Gas Liquor%	Tar%	Tar Oil%
Antimony	50.0	46	3.75	1.26
Arsenic	27.0	66.6	2.26	4.26
Boron	92.0	6.6	1.496	.004
Bromine	10.86	89.0	.14	--
Cadmium	52.0	46.0	.90	2.1
Fluorine	56.0	43.917	.08	.003
Lead	93.6	2.064	4.33	.016
Mercury	50.93	40.30	8.12	.66
Nickel	99.564	0.41	.03	.006
Zinc	100%	--	--	--

Note that bismuth, gallium, germanium and selenium are listed as trace constituents in the coal. However, none of the reports referenced addressed these elements and they are necessarily excluded for that reason. The trace element values are based on the high range numbers in Table 4-3.

4.1.7 Lock Gas

The lock gases for both the coal lock and the ash lock are discussed in Chapter 6.

4.2 POTENTIAL EFFLUENTS

4.2.1 Major Pollutants

The major process streams from this section are sent to downstream processing; none are discharged to the environment at this point. There are, however, various points within the area where the potential for minor quantities of particulate or gaseous emissions exists. These four points are the coal feed bin, the coal lock, the ash lock and the ash quench system. The ash and coal lock discharges are discussed in Chapter 6.

Emissions from the coal bin will include coal dust and other coal particulates caused by dumping the coal from the feed conveyor into the feed bin. Dust could be a major local problem. Potential emissions from the ash quench system will include fine ash particles, large clinkers, steam and some non-condensable gases formed during the quenching process. Blowdown from steam generating equipment associated with the gasifier will be discharged into the plant water system.

Other possible contaminant sources are leaks around heat exchangers, vessels and pumps. The composition and amount of effluents emitted will vary from day to day and will be dependent upon the level of plant maintenance. These items cannot be estimated at this time but their possible presence should be taken into consideration.

4.2.2 Trace Constituents

No information is available on the distribution of trace elements in the atmospheric discharge streams. The temperatures and

pressures involved at the discharge points together with data from the trace element studies would lead one to believe that little, if any, trace elements would be contained in those streams.

4.3 CONTROL METHODS

4.3.1 Proven Methods

Control systems for the coal feed bin emissions were not mentioned in the El Paso EIS. The WESCO EIS did state that dust hoods coupled to baghouses would be used to control particulates emitted from the coal transfer point. Estimated total particulates to the atmosphere for this system are 0.97 lb/hr.

Control of emissions for the ash quench system will involve a two stage process. The steam, gases, ash dust and clinkers will initially be passed through a wet cyclone for removal of the clinkers and some dust. The remaining material will then go to a condenser where the steam is condensed. Most of the ash dust will come out in the condensate. The final fate of the non-condensable gases is not known, since no information concerning their composition or volume is available. Observations made about the ash quench operation at the Sasol plant revealed that the vapor gas generated during quench is mostly steam. No particulate emission data for the system are available.

4.4 PROCESS MODIFICATIONS

There is no direct discharge to the environment from the gasifier section which might suggest modifications to the actual process equipment. The most effective form of emission reduction would involve the improvement of "downstream" pollution control equipment. Controls on the coal feed system may be warranted from the standpoint of worker health.

REFERENCES

1. El Paso, "Draft Environmental Impact Statement," El Paso Coal Gasification Project, July 1974.
2. WESCO, "Final Environmental Impact Statement - WESCO Coal Gasification Project, 1975.
3. Exxon, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Gasification; Section I: Lurgi Process," EPA 660/2-74-009-C, July 1974.
4. EPA, "Fate of Trace Constituents of Coal During Gasification," EPA 660/2-73-004, August 1974.
5. Pittsburgh Energy Research Center, "Trace Elements and Major Component Balances Around the Synthene PDU Gasifier," EPA 600/2-76-149 June 1976.
6. EPA Communication.

5. FUEL GAS PRODUCTION

5.1 STREAM FLOWS

The fuel gas burned to provide steam, electric power, and air compression for the plant is obtained from a process train consisting of 10 air blown Lurgi gasifiers. These units produce 2,800 MMBTU/HR of fuel gas with a higher heating value of 193.9 BTU/SCF. The process scheme for the fuel gas production area is shown in Figure 5-1.

The gasifiers operate similar to those described in Chapter 4 except for the use of air rather than oxygen.

5.1.1 Coal Feed

Sized coal from the coal blending and preparation area is fed to the gasifier coal bunker at 415,587 pounds per hour. The breakdown of this feed into major components is given in Tables 5-1 and 5-2.

Table 5-1. MOISTURE AND ASH-FREE COAL COMPONENT ANALYSIS

<u>Component</u>	<u>wt %</u>	<u>lb/hr</u>
Carbon	76.26	204,417
Hydrogen	5.56	14,967
Nitrogen	1.32	3,538
Sulfur	1.07	2,868
Oxygen	15.74	42,193
Trace Compounds	<u>0.03</u>	<u>80</u>
TOTAL	100%	268,063

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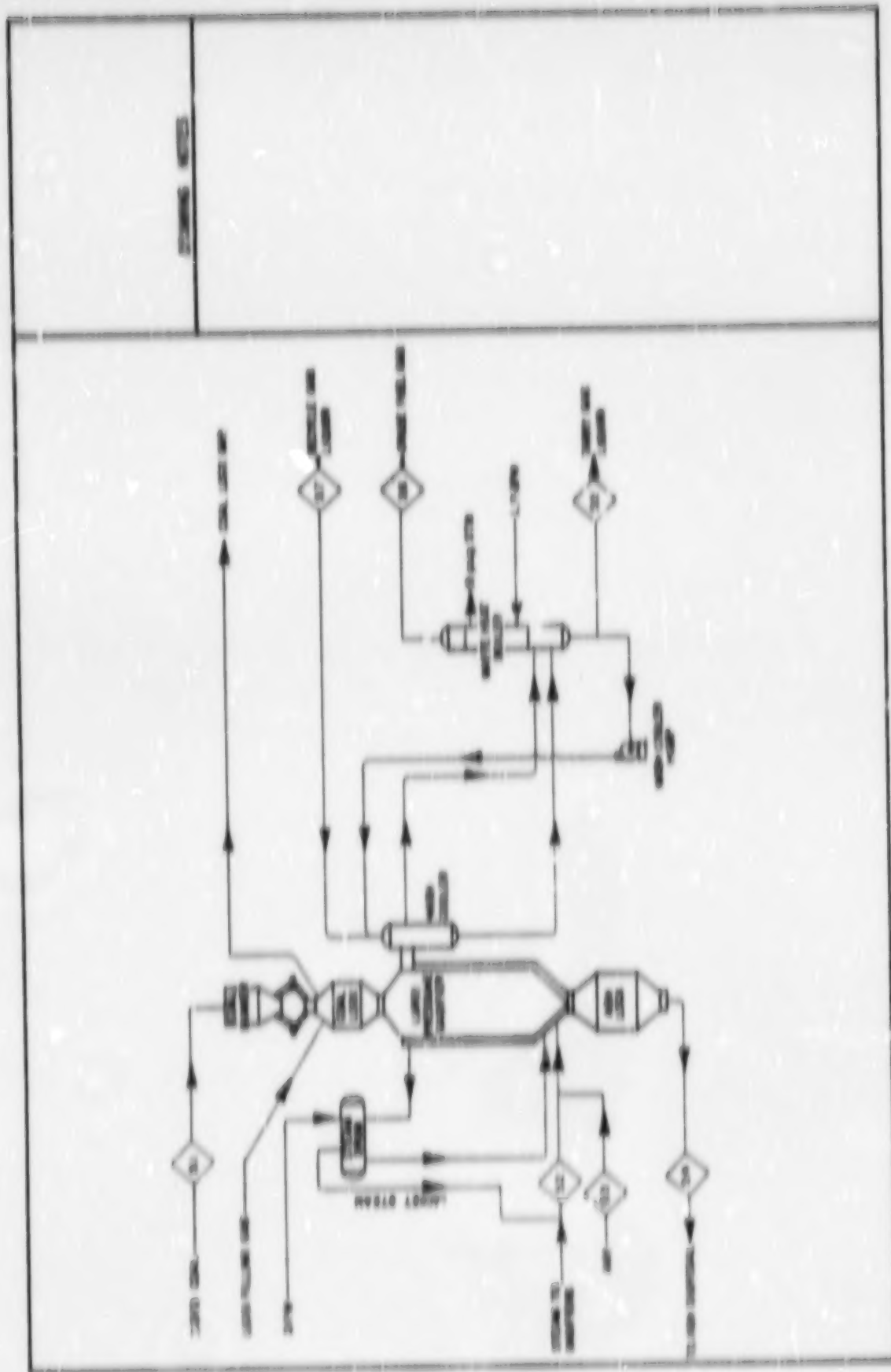


Figure 5-1. FLOW SCHEME FOR FUEL GAS PRODUCTION

Table 5-2. MATERIAL BALANCE FOR FUEL GAS PURIFICATION

Stream Label Component	5.1 lbs/hr	5.2 lbs/hr	5.3 lbs/hr	5.4 lbs/hr	5.5 lbs/hr	5.6 lbs/hr
CH_4						247,503
H_2						1,053
C_2H_6						2,436
C_3H_8						181,475
N_2						17,429
CO_2						31,250
C_2H_4						4,342
$H_2 + Ar$			406,563			401,113
O_2			121,100			
Total Dry Gas			528,363			882,963
Water	67,522	258,739		51,946	→	285,634
Coal (B&E)	258,353			4,355		
Ash	81,012			81,012		
Reagents						4,355
Tar Oil					2,578	6,072
Tar					14,307	1,583
Crude Phenols					37	1,563
H_2						3,771
TOTAL	415,587	258,739	528,363	125,177		1,386,270

Table 5-2 is an estimate of flow rates for various trace constituents in the coal feed.

Table 5-3. TRACE ELEMENTS
(Pounds per Hour)

Element	From	To
Antimony	0.32	.08
Arsenic	0.80	.027
Bismuth	0.05	0.0
Boron	40.21	18.08
Bromine	4.82	0.11
Cadmium	0.11	.06
Fluorine	209.08	83.61
Gallium	2.14	0.13
Germanium	0.13	0.27
Lead	1.07	0.37
Mercury	0.08	0.54
Nickel	8.04	0.80
Selenium	0.05	0.27
Zinc	7.24	0.29

5.1.1 Steam and Air

Steam to the gasifier comes from conventional steam generating equipment plus steam produced in the gasifier cooling jacket. This steam is fed to the gasifier at 550 psig and 750°F.

Air is dried and compressed to 360 psia before being supplied to the gasifier at a rate of 629,763 pounds per hour.

5.1.3 Untreated Fuel Gas

The crude fuel gas is cooled and washed immediately following its exit from the gasifier, and is then further cooled in a waste heat boiler which produces 15 psig steam. After leaving the area, the gas is subjected to additional cooling and then to treating for sulfur removal. The composition of the fuel gas as it leaves the fuel gas production area is estimated to be as shown in Table 5-2.

5.1.4 Tarry Gas Liquor

Recycle gas liquor from the gas liquor separation plus the tar, tar oils and phenols condensed from the gas in the wash cooler and waste heat boiler comprise the tarry gas liquor stream. This stream is sent to the gas liquor separation area for tar and tar oil removal. Flow rates for the major components except water are given in Table 5-2.

Besides these major components, this stream will also contain varying amounts of CO_2 , H_2S , HCN , plus coal dust and ash. Not enough data was available to estimate the amounts of these constituents. The composition of the tar and tar oil from the fuel gas producer is not known for the El Paso design. As with the tar products from the gasifier, an estimate can be made using data from runs on Lurgi gasifiers at Westfield, Scotland. These data are presented in Tables 8-3 and 8-4.

5.1.5 Ash

The ash discharge and quench system for the fuel gas producers is the same as that for the high BTU gasifiers. Refer to Section 4.1.5 for discussion.

Flow rates and stream compositions of the ash from the fuel gas producer are given in Table 5-2. A component breakdown for the unreacted coal and ash is shown in Table 5-4.

Table 5-4. ASH STREAM COMPONENT ANALYSIS

<u>Unreacted Coal Analysis</u>	<u>Rate lb/Hr</u>
Carbon	3210.0
Hydrogen	236.0
Nitrogen	66.8
Sulfur	46.0
Oxygen	662.0
<u>Ash Analysis</u>	
SiO_2	49,607
Al_2O_3	20,003
Fe_2O_3	4,002
CaO	3,129
MgO	720
K_2O	640
Na_2O	1,200
TiO_2	720

A breakdown of the ash water quench stream is given in Table

5-5.

Table 5-5. ASH WATER QUENCH STREAM

<u>Source</u>	<u>Rate lb/hr</u>
Blowdown	110,338
C-T Blowdown	135,500
Contaminated Gas Liquor	135,500
Process Condensate	413
Utility Water	41,193
TOTAL	422,950

5.1.6 Trace Elements

The trace element background information contained in Chapter 4, is also applicable here. The trace element analysis for each stream in the fuel gas section is given below.

Table 5-6. TRACE ELEMENTS - FUEL GAS PRODUCER ASH
(Pounds per Hour)

<u>Elements</u>	<u>Maximum Rate</u>
Antimony	.16
Arsenic	.216
Boron	36.99
Bromine	.82
Cadmium	.057
Fluorine	117.08
Lead	1.00
Mercury	.041
Nickel	0.004
Zinc	7.24

Table 5-7. TRACE ELEMENTS - TARRY GAS LIQUOR (STREAM 5.5)
(Maximum Rates, Pounds per Hour)

<u>Element</u>	<u>Water</u>	<u>Tar</u>	<u>Tar Oil</u>
Antimony	144	.0108	.0012
Arsenic	.532	.0162	.0102
Boron	2.81	0.54	.00016
Bromine	4.28	.0060	--
Cadmium	.049	.000891	.000793
Fluorine	91.82	.150	.00188
Lead	.022	.042	.00005
Mercury	.032	.0058	.00016
Nickel	.032	.00217	.000144

Table 5-8. TRACE ELEMENTS - TAR, TAR OIL IN GAS STREAM (5.6)
(Maximum Rates, Pounds per Hour)

Element	Tar	Tar Oil
Antimony	.0012	.0028
Arsenic	.0018	.0238
Boron	.080	.00112
Bromine	.00067	--
Cadmium	.000099	.0016
Fluorine	.0167	.0044
Lead	.0046	.00012
Mercury	.00064	.00036
Nickel	.00024	.00034

NOTE: The trace element values are based on the high range numbers,
Table 5-3.

5.1.7 Lock Gases

The lock gases for both the coal lock and the ash lock are discussed in Chapter 6.

5.2 POTENTIAL EFFLUENTS

5.2.1 Major Pollutants

Pollution sources in this section include the coal bunker, coal lock, ash lock and the ash quench system. All process streams and major waste streams exit the area for further processing and separation. None are discharged to the environment at this point. Emissions from the coal and ash lock consist of residual pressurizing gas forced out by the incoming coal and ash. These streams are estimated and discussed in Chapter 6. Emissions from the coal bunker will be coal dust particles generated by transfer of coal from the conveyor to the bin. The particle size or concentration of dust in the air at that point is not known.

The ash quench system generates large volumes of steam containing fine ash particles, clinkers and non-condensable gases generated from reactions involving organics contained in the water and unreacted coal in the ash. The volume of steam, dust and clinker loading and non-condensable gas composition and volume are not known.

6.2.2 Trace Constituents

No information is available on the trace constituents in these vent streams.

6.3 CONTROL METHODS

6.3.1 Proven Methods

Control of the particulates from the coal transfer for the WESCO case will be obtained by the use of dust collection hoods and baghouses. No information concerning control methods was given for the El Paso design, but it is assumed that the same type of control could also be used here. Since baghouses are very efficient, the total particulates emitted to the atmosphere at the exit of the baghouse is estimated to be about 0.23 lb/hr.

The steam-ash stream generated by the ash quench will initially be routed to a wet cyclone for removal of the larger clinkers carried by the stream. The remaining material will be sent to a cooling water condenser where the steam will be condensed and returned to the ash transfer sluiceway. It is expected that almost all of the fine ash particles would remain in the condensate. The fate of the non-condensable gases is not known. Recommendations for their disposal cannot be made since information is not available on the composition or volume of this stream.

5.4 PROCESS MODIFICATIONS

No modifications are suggested from the standpoint of environmental control. Hooded fans may be required at local points to avoid worker exposure to gases and dusts.

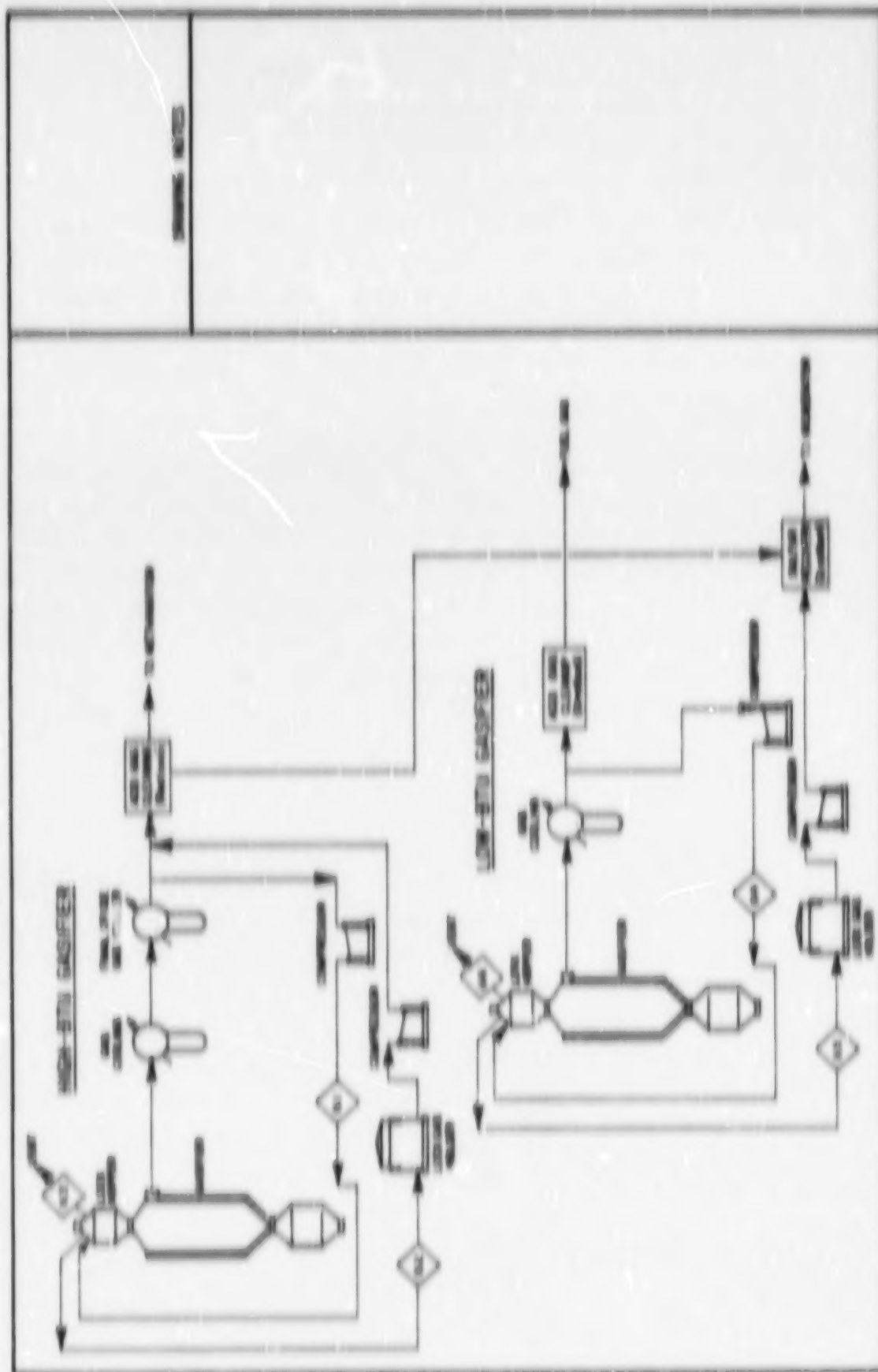
6. LOCK HOPPER GASES

6.1 STREAM FLOWS

In the Lurgi process, coal is fed to the gasifier in a cyclic operation using a pressurized hopper. The pressurizing gas must be vented each time the feed lock hopper (FLH) is re-charged. Normal charging frequency is 15 to 30 minutes.⁽²⁾ Ash is discharged from the bottom of the gasifier through another lock hopper which must be vented. Ash hopper discharge cycles are about 20 minutes.

Composition of the FLH pressurizing gas can be highly variable, depending upon the source utilized. In the El Paso design, crude gas is withdrawn just before the final crude gas cooler and compressed directly into the FLH. For the low BTU gasifiers, the FLH gas is withdrawn after the final fuel gas cooler. The two FLH flow schemes are shown in Figure 6-1.⁽¹⁾ Gas compositions going to the FLH are given in Table 6-1. Flow rates are not given by El Paso, but can be estimated as follows. Total coal feed to the high BTU gasifiers is given as 1,936,480 lb/hr. If it is assumed that the bulk weight is approximately 60 lb/ft³, then 32,000 ft³/hr is the volumetric charging rate.

The lock hoppers probably cannot be filled completely. If 90% filling is assumed, and 30% void volume in the coal, then the pressurant gas volume will be 11,600 ft³/hr at a pressure of 445 psia. With a molecular weight of 21, this results in a gas flow of approximately 20,000 lb/hr for initial charging of the hopper. Addition of gas during the run to replace the bulk volume of coal-plus-gas entering the gasifier would require another 49,000 lb/hr. The total of 69,000 lb/hr represents 3 to 4% of the entire crude gas make. This figure corresponds to that quoted in Ref. (2). Similarly, it can be computed that the mass flow rate of FLH gas for the low BTU gasifiers will be approximately 13,000 lb/hr.



SHOWN NOTES

Figure 6-1. FLOW SCHEME FOR THE FEED LINE 10054

Table 6-1. COMPOSITIONS OF COAL FEED LOCK HOPPER PRESSURIZING GAS

Constituents	Volume Percent, Dry Gas					
	A	B	C	D	E	F
CO ₂	28.03	14.83	28.90	48.88	77.53	98.42
H ₂ S + COS	0.37	0.24	.32	0.42	0.76	
C ₂ H ₄	0.40	0.28			0.29	0.78
CO	20.20	17.48	19.55	13.96	14.06	0.41
H ₂	38.95	23.27	30.81	27.84	2.01	0.39
CH ₄	11.13	8.07	11.09	7.95	4.6	1.85
C ₂ H ₆	0.61	0.37	1.01	0.72	0.47	1.15
N ₂	0.31	38.50	.32	0.23	0.28	

- (1)
A El Paso - High BTU Gasifiers
B El Paso - Low BTU Gasifiers
C WESCO - Fluor Corp. design
D WESCO - Fluor Corp. design
E WESCO(3)
F NGPL(4)

The original WESCO design estimated a crude gas composition given in Column C, Table 6-1. Presumably this would provide the lock hopper feed. However, the FLH vent gas composition was given as Column D. No explanation was provided for the shift in concentrations. In the WESCO environmental impact statement⁽³⁾ the pressurizing gas was changed to CO₂ (source not given) and the vent gas composition given as Column E, Table 6-1.

In the Natural Gas Pipeline Co. design⁽⁴⁾ FLH pressurizing gas is obtained from the Rectisol plant vent stream. Composition of this gas is listed in Column F, Table 6-1.

In summary, the composition of the coal FLH pressurizing gas can be widely variable from one plant to the next, depending upon the plant designer's choice of a source for the gas. Molecular weight could vary from 21 to 44. Volumetric pressurant requirements will be unaffected by changes in composition. Weight flow rates based on Columns A and B, Table 6-1, are given in Table 6-2.

Flowrates in Table 6-2(A) are based on the assumption that gas is continually added to the FLH during a run in order to maintain the pressure slightly above that in the gasifier. This procedure is specified in the WESCO design. If, instead, the mode of operation is such that no gas is added during a run, gases from the top of the gasifier will back flow through the entering coal stream to fill the void being created in the FLH. Material balances given for the cooling section in the El Paso design indicate that this type of operation is planned. The 49,000 lb/hr gas flow required to replace the coal bulk volume would then not appear in stream 6.1, Figure 6-1, but would pass from the gasifier directly to the FLH. For the present analysis it is assumed that in passing countercurrently through the incoming coal these gases would be cooled by heat exchange with the coal, and that tars, oil and water would condense on the coal. The composition of gas in the FLH

Table 6-2. MATERIAL BALANCES FOR LOCK HOPPER GAS FLOWS

A. Gas Added During Run

STREAM NUMBER	6.1	6.2	6.3	6.4	6.5	6.6
COMPONENT	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR
CO ₂	40,086	38,918	1,168	3,652	3,501	152
H ₂ S + COS	412	400	12	44	42	2
C ₂ H ₄	367	356	11	39	36	1
CO	18,393	17,848	535	2,736	2,622	114
H ₂	2,551	2,477	74	263	251	11
CH ₄	5,805	5,636	169	456	432	19
C ₂ H ₆	593	576	17	64	62	2
H ₂ + Ar	358	348	10	6,039	5,788	252
Naphtha	176	171	5	64	62	2
Water	561	545	16	25	24	1
TOTAL	69,292	67,275	2,017	13,382	12,828	556

B. No Gas Added During Run

STREAM NUMBER	6.1	6.2	6.3	6.4	6.5	6.6
COMPONENT	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR	LBS/HR
CO ₂	11,423	38,918	1,168	1,080	3,501	152
H ₂ S + COS	116	400	12	13	42	2
C ₂ H ₄	104	356	11	12	38	1
CO	5,240	17,848	535	809	2,622	114
H ₂	727	2,477	74	77	251	11
CH ₄	1,653	5,636	169	135	432	19
C ₂ H ₆	168	576	17	19	62	2
H ₂ + Ar	102	348	10	1,786	5,788	252
Naphtha	171	171	5	19	62	2
Water	296	545	16	7	24	1
TOTAL	20,000	67,275	2,017	3,960	12,828	556

at the end of the coal feeding cycle would therefore be essentially the same as before. Flow rates for streams 6.3 and 6.2, Figure 6-1, would be unchanged. A similar situation would prevail for the low-BTU gasifier FLH streams. Material balances for this type of lock hopper operation are given in Table 6-2(B). The amount and composition of gas vented from the system will be the same in either case, and only the internal flow rate for pressurizing gas will be affected.

Ash is discharged from the bottom of the gasifier in a sequence of operations similar to that for the FLH. First the top ash lock cone valve is closed, isolating the ash lock chamber. High pressure gases in the ash lock at this point are mainly steam. The chamber is vented to a close coupled direct contact condenser, where the steam is condensed with a water spray. The bottom ash lock valve is then opened and the ash falls out. After the ash is dumped, both cone valves are closed and the ash lock chamber is repressurized with steam. The top ash lock valve is opened and ash flow from the producer is re-established.

As in the case of the coal feed lock hopper, it is possible that a different operating procedure could be used, in which the ash lock chamber is not repressurized before reopening the valve to the gasifier vessel. In that case gases from the gasifier would flow into the ash lock hopper. Venting of the ash hopper on the next cycle could then result in the emission of some of these gasifier gases.

Several variations are possible in handling the ash as it drops from the ash lock chamber. In one design, the ash drops into circulating "mud water" in an ash quench chamber directly below the ash lock. In the El Paso design the ash is apparently discharged dry at about 200° C into a sluice launder where it is completely quenched and flushed away by a water stream. Since the gasifier bottom temperature is around 500°C, it is assumed that partial cooling is accomplished by water spray

before dropping into the sluice launder. Steam generated in the quenching will be condensed either in the direct contact condenser coupled to the ash lock valve or in a condensing vessel above the sluice launder. To cool the ash from 500 to 200°C, assuming a specific heat of 0.2, would require approximately 48,000 lbs of water per hour.

During the ash quenching, large amounts of ash dust are generated and entrained in the steam passing to the condensers. Some noncondensable gases may be generated also by reaction between unburned char and steam or by thermal cracking of organic contaminants in the quenching water. The water spray in the condenser provides a wet scrubbing action to remove most of the ash dust from the non-condensable gas which must be vented. Estimated flow rate is 477,000 lb/hr of ash. Approximately 64,000 lb/hr of water will be flashed to steam in the two-step quench process. No information is available for estimating the amount of noncondensable gases formed or the amount of particulates carried by this stream.

6.2 POTENTIAL EFFLUENTS

6.2.1 Major Pollutants

If all FLH pressurizing gases are vented to the atmosphere, then Table 6-2, and Figure 6-1 may be used to calculate the potential emissions of major pollutants. Since volumetric requirements are constant regardless of composition, inspection of Table 6-1 shows that the use of crude gas for FLH pressurizing (as in the El Paso design) represents a worst case for potential emissions of carbon monoxide and methane. Hydrogen sulfide emissions are worst in the WESCO design (gas source not defined in flow sheet), and non-methane hydrocarbons are maximized in the HGPL design (using Rectisol vent gases). Worst-case emissions for each component, assuming the El Paso design but without recycling, are summarized in Table 6-3.

Table 6-3. WORST-CASE POTENTIAL EMISSIONS FROM FEED LOCK HOPPERS

<u>Component</u>	<u>Emissions, Lbs/Day</u>	<u>Emissions, Tons/Yr</u>	<u>Emissions, Lbs/10⁶ BTU Coal</u>
H ₂ S	11,000	2,000	0.022
CO	509,000	92,900	1.0398
CH ₄	152,000	27,700	0.310
NMH	40,800	7,450	0.083

Table 6-4. FEED LOCK HOPPER EMISSIONS WITH GAS RECYCLE

<u>Component</u>	<u>Emissions, Lb/Day</u>	<u>Emissions, Tons/Yr</u>	<u>Emissions, Lbs/10⁶ BTU Coal</u>
H ₂ S	336	61	0.001
CO	19,300	2,790	0.031
CH ₄	4,460	814	0.009
NMH	1,180	215	0.002

Uncontrolled sulfur emissions from venting all FLH gases are approximately 2000 tons per year. This is a factor of almost 100 more than some estimates (p. 3-14, Ref. 9). Hydrocarbon emissions would also be about ten times larger than estimated in Ref. 9. If the FLH gas is recycled, as in the El Paso design, and only the residual gas remaining in the FLH is vented to the atmosphere, then total emissions would be as given in Table 6-4. These vents have not been shown on the El Paso flow sheets. Even with recycling, the sulfur emissions would be over twice the value listed in Ref. 9. Venting of FLH gases will also be a major source of carbon monoxide emissions, which were omitted from the Table 3-4 of Ref. 9. It should be noted that even if CO_2 is used as the FLH gas source, blowback from the gasifier after the hopper is emptied could result in appreciable emissions when the hopper is vented.

Vent gases from the lock hopper will contain some entrained coal dust. Without actual data from an operating gasifier it is impossible to estimate the quantity involved. Amounts are likely to be a function of whether the lock hopper is completely emptied during the charging cycle, rate of depressurization, size distribution of coal feed, and geometric arrangement of vent openings.

Noncondensable gases generated in the ash quench chamber will contain ash dust. Quantities of gas and dust in this stream are unknown.

6.2.2 Trace Constituents

Trace constituents in the FLH vent gases should be the same as in the source stream. No additional contaminants will result from the pressurizing process, except for entrainment of coal dust.

6.3 CONTROL METHODS

6.3.1 Proven

Since the major control methods for FLH vent gases consist of variations in process design which have not been tried, it is perhaps misleading to talk about proven methods. The discussion in this section, however, will concern design variations which are believed to have no known technical problems. Several choices are available both for the source of the pressurizing gas and for the disposition of the gas when venting the lock hopper.

Among the choices which might be considered for a gas source are (1) raw crude gas, (2) clean crude gas, (3) product gas, (4) Rectisol vent gas, (5) nitrogen from air plant. Any of these sources could provide sufficient quantities of gas chemically compatible with the coal in the lock hopper. Use of nitrogen or incinerator tail gas can probably be disqualified because it would introduce nitrogen into the product gas stream. The use of any slip stream from the product gas flow, whether raw crude, clean crude or final product gas, will result in some emission of this gas, even if most of it is recycled. On the other hand, if CO_2 from the Rectisol vent is used, this is a stream which is vented anyway, so total emissions may not be changed appreciably. All process equipment between the gasifier and the slip stream point must be oversized to handle the approximately 30% of lock gas which will pass into the gasifier with the coal feed. Therefore there is an economic incentive to locate the bleed point as close to the gasifier as possible. If Rectisol vent gas is used, then all equipment through the CO_2 absorption train must be oversized. Another economic factor is that bleeding from a high pressure stream rather than a low pressure stream will reduce compression costs.

In disposing of the FLH vent gases, at least four alternatives are available: (1) Recycling, (2) Venting to atmosphere, (3) Use as plant fuel gas, (4) Incineration. Not all disposal options could be combined with every source option. For instance, if the source is CO_2 vent gas,

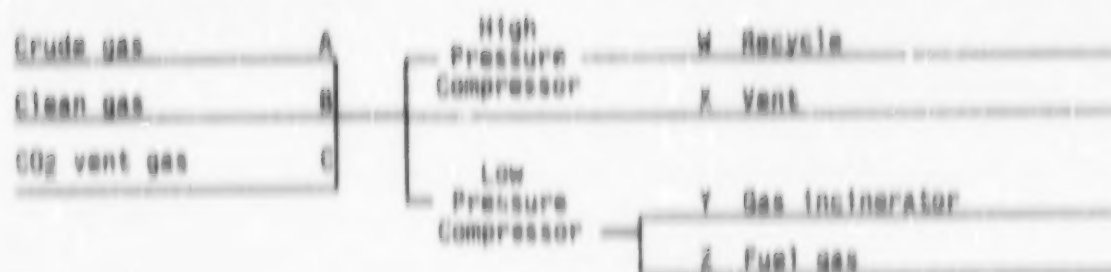
It would obviously be impossible to dispose by burning as fuel. Figure 6-2 illustrates the various combinations of source and disposal alternatives with a brief summary of strengths and weaknesses. Since there would be relatively little difference between using final product gas or clean gas prior to methanation, only "clean gas" is listed. The ultimate choice must be based on considerations involving the rest of the plant design. For instance, if gas is being burned as a plant fuel, then passing a slipstream through the lock hopper before burning will not increase overall plant emissions. In this case, recycle compressors are not needed. If fuel gas (either crude or cleaned) is chosen to pressurize the lock hopper, there will be an economic incentive to recover the majority of the gas by either recycling or using as fuel, so that direct venting is unlikely. If CO_2 is used, then direct venting may be acceptable because this gas would be vented anyway. In the El Paso design, Figure 6-1, the low-BTU lock hopper vent gas is injected into the low pressure Stratford unit which processes acid gas from the Rectisol unit. This automatically provides a clean fuel to fire the off-gas incinerator.

Although most of the FLH gas can be collected and disposed of by one of the options discussed, there will be a residuum of gas in the hopper when it is opened to receive a new coal charge (the hopper cannot be evacuated, it can only be bled down to some pressure slightly above atmospheric). During the coal transfer this residual gas will be displaced equal to the volume of coal being loaded. Several plant designs have discussed the use of exhaust hoods and vent fans on the gasifier to prevent local escape of these gases, as e.g. Figure 6-3. This type of control does not affect the net release to the environment unless the collected gases are then incinerated. The amount of gas escaping in this way should be only about 3% of the pressurant requirements. Flow rates are given as streams 6.3 and 6.6 in Figure 6-1 and Table 6-2. In the WESCO design it was stated that these gases would be collected by exhaust fans and vented from stacks, 150 to 300 ft. high. The flow would be 99.95 air at a rate of 2,934 tons/day. Estimated H_2S concentration was 5-10 ppm. If either clean crude gas or CO_2 from the Rectisol vent is used, the H_2S level

Figure 6-2 FEED LOCK HOPPER GAS ALTERNATIVES

Possible Sources

Disposal Options



Combinations

Remarks

AW	El Paso design - requires oversize gas coolers only
AX	Greatest pollution plus economic penalty for loss of gas
AY	Less pollution but same economic penalty as AX
AZ	No oversize required, no pollution penalty if crude is to be used as fuel anyway
BW	Entire process train to bleed point must be oversized
BX	Economically unsound because recycling should be cheaper than increasing output of entire plant
CX	Even greater economic penalty than BX
CZ	Represents good control where product gas is used as fuel
DW	Increase equipment size with no benefit over CX - does not change total vent flow
CX	Since gas will be vented whether used for lock hopper or not, have not increased pollution load
CY	Not reasonable
CZ	Not practical

THE LURGI GASIFIER

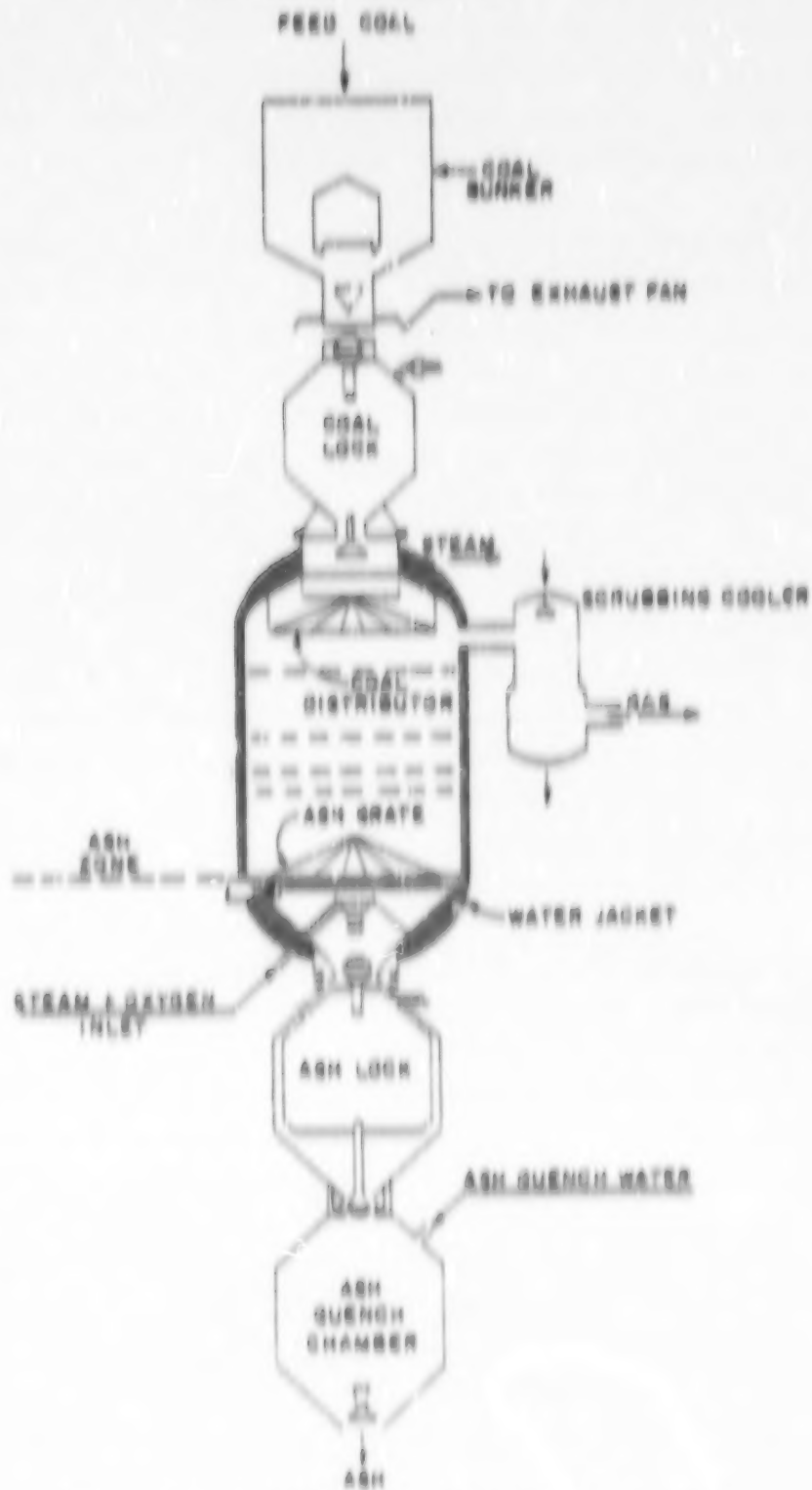


Figure 6-3 GASIFIER SCHEMATIC WITH EXHAUST FAN

should be much lower. There may be some blowback of gas from the gasifier into the lock hopper during production, so that even if CO_2 is used to pressurize, there may be some H_2S in the vent stream. The amount of any such blowback is impossible to estimate.

Localized control of vent gases from the ash lock quenching and ash dumping operations can be accomplished also by hoods and exhaust fans. The exhaust fans for both the coal lock and ash lock can be equipped with wet cyclone scrubbers to reduce particulate concentration before being vented from stacks. The WESCO EIS contained an estimate of particulate emissions from the lock exhaust fans with cyclone scrubbers which amounted to only 0.1 lb/hr for the coal lock and 0.2 lb/hr for the ash lock.

6.3.2 Potential

Potential methods are considered to be those requiring some process development before they could be utilized in a plant design. Since adequate control can be achieved with the best of the methods discussed, no further development is required.

6.4 PROCESS MODIFICATIONS

Most of the control methods discussed are actually process modifications rather than end-of-pipe methods of treatment. Additional modifications which could be developed would include the feeding of the exhaust vent streams to the intake air for air blown gasifiers, gas turbines, or steam boilers. Since the potential emissions involved are so small to begin with, there is little incentive to spend effort in investigating such modifications.

It is apparent that total venting of lock hopper gases could be a significant source of emissions if the gas is obtained from an internal process stream. All designs utilizing such internal streams should require either recycling or routing to a pollution control unit.

References

1. El Paso, "Second Supplement to Application of El Paso Natural Gas Company for a certificate of Public Convenience and Necessity," Docket No. CP73-131, Federal Power Commission, October 1, 1973.
2. WESCO, "Amended Application for Certificate of Public Convenience and Necessity," Docket No. CP73-211, Federal Power Commission, November 1973.
3. WESCO, "Final Environmental Statement - WESCO Coal Gasification Project-1975.
4. NGPL, "Environmental Assessment of a Coal Gasification Complex in Dunn County, North Dakota," September 1974.
5. Wyoming Coal Gas, "Applicant's Environmental Assessment for a Proposed Coal Gasification Project, Campbell and Converse Counties, Wyoming," October 1974.
6. Exxon, "Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Gasification; Section I: Lurgi Process," EPA-660/2-74-009-C, July 1974.
7. Booz-Allen, "Comparative Assessment of Coal Gasification Emission Control Systems," EPA Contract No. 68-01-2532, October 1975.
8. Woodall-Duckham, "Trials of American Coals in a Lurgi Gasifier at Westfield, Scotland," ERDA report FE-105, November 1974.
9. EPA, draft document, "An Investigation of the Best Systems of Emission Reduction for Coal Gasification Plants",

7. SHIFT REACTION

The shift reaction section of the Lurgi high-Btu coal gasification process is designed to adjust the H_2/CO ratio of the synthesis gas to that required in the methanation section. This is accomplished by the catalyzed reaction of CO and H_2O according to Equation 7-1.



7.1 STREAM FLOWS

The process flow scheme and the material balance for the shift reaction section are given in Figure 7-1 and Table 7-1, respectively. Raw gas from the gas production section is split into two streams with approximately 55 percent being sent to the shift reaction section. This stream is cooled in a waste heat boiler that generates 60 psig steam. The water condensed from the raw gas is sent back to the gas production section for use as a raw gas quench liquor.

After leaving the waste heat boiler, the raw gas undergoes the reaction shown by equation 7-1 in two catalytic shift reactors. The hot exit gas from each reactor is cross exchanged with the reactor inlet gas to maintain the proper inlet temperature to each reactor. The shifted gas is then directed to the gas cooling section for further processing.

7.2 POTENTIAL EFFLUENTS

The effluent streams from the shift reaction section include:

- Shifted gas
- Process Condensate
- Waste Heat Boiler Blowdown
- Spent Catalyst
- Fugitive Emissions (equipment malfunctions)

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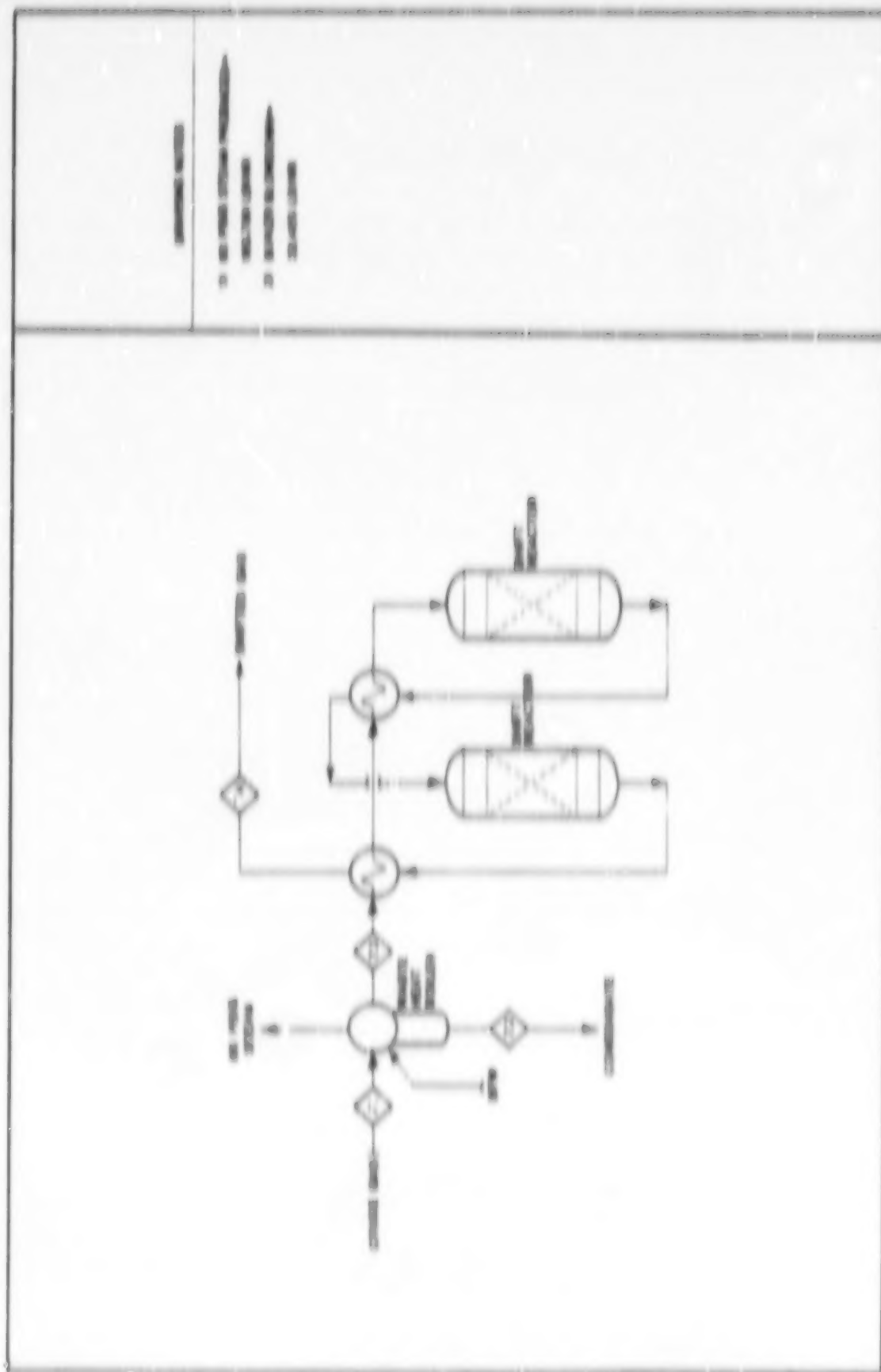


Figure 7-1. FLUID SCHEME FOR THE SHIFT REACTION SECTION

Table 7-1. MATERIAL BALANCE FOR THE SHIFT REACTION SECTION

Stream Number		7.1	7.2	7.3	7.4
Stream Description		Crude Gas From Gas Production	Condensate to Gasifier Quench	Crude Gas to Shift Reactors	Shifted Gas
Gas Phase, lb/hr					
Component	Molecular wt.				
CO ₂	44.010	729,158	=	720,545	1,096,707
CO	28.010	334,465	=	336,437	95,029
CH ₄	16.042	105,537	=	105,532	105,532
H ₂ S	34.082	7,403	=	7,280	7,280
C ₂ H ₆	30.052	6,710	=	6,710	6,710
C ₃ H ₈	44.097	10,789	=	10,788	10,788
C ₄ H ₁₀	58.12	6,486	=	6,486	6,486
N ₂ +Ar	28.013	46,401	=	46,401	63,632
H ₂	2.016	762,763	=	511,730	357,763
H ₂ O	18.016	10,939	=	10,939	10,939
Naphtha	114.216	15,314	=	15,314	15,314
Tar Oil	186.354	3,999	=	3,999	3,999
Tar	94.108	4,991	=	4,991	4,991
Phenol	94.108	9,640	=	9,640	9,640
NH ₃	17.032				
Total Gas, lb/hr		2,055,395	=	1,795,812	1,795,812
Liquid Phase, lb/hr					
Component	Molecular wt.				
H ₂ O	18.016	=	251,013	=	=
Tar Oil	186.354	=	*	=	=
Tar	94.108	=	*	=	=
Phenol	94.108	=	*	=	=
Dissolved NH ₃	17.032	=	*	=	=
Dissolved CO ₂	44.010	=	8,613	=	=
Dissolved H ₂ S	34.082	=	123	=	=
Dissolved CO	28.010	=	28	=	=
Dissolved CH ₄	16.042	=	5	=	=
Total Liquid, lb/hr		=	259,782	=	=
Temperature, °F		370	338	338	330
Pressure, psia		430	450	450	400

* present, but quantity unknown

The major pollutants in each of these effluent streams are addressed in Section 7.2.1 while the presence of trace constituents is discussed in Section 7.2.2.

7.2.1 Major Pollutants

Shifted Gas. The shifted gas contains the same pollutants as the inlet raw gas stream to the shift reaction section. These pollutants include:

- H_2S , COS and organic sulfur compounds
- NH_3
- Tars
- Tar Oils
- Phenols
- Naphtha

The anticipated composition of the shifted gas is shown below.

<u>Component</u>	<u>Vol%</u>	<u>Component</u>	<u>Vol%</u>
CO_2	28.3	H_2	36.8
CO	3.8	H_2O	22.8
CH_4	7.5	Naphtha	0.1
$H_2S + COS$	0.2	Tar Oil	0.1
C_2H_6	0.3	Tar	<0.1
C_3H_8	0.4	Phenol	0.1
$N_2 + Ar$	0.2	NH_3	0.6

Process Condensate. The condensate from the waste heat boiler contains dissolved CO_2 , CH_4 , CO, H_2S and H_2 . In addition, a portion of the heavy hydrocarbons present in the inlet raw gas stream would probably be found in this condensate, although these components are not shown in the material balance given in Table 7-1.

Boiler Blowdown. The waste heat boiler in the shift reaction section uses softened water for boiler feed. This inlet stream contains some dissolved solids, consisting mainly of Na^+ , SO_4^{2-} , Cl^- , CO_3^{2-} and silicates. Only very small amounts of Ca^{++} and Mg^{++} are present. To prevent scaling of the boiler tubes, a portion of the boiler water is removed as blowdown. Since the boiler operates at approximately seven cycles of concentration, this blowdown stream contains seven times the inlet concentration of each ionic species. Since no other pollutants are anticipated to be present in the boiler blowdown stream, it is directed to the plant cooling system for use as makeup water.

Fugitive Emissions. Fugitive emissions from the shift reaction section arise from leaks around valves, flanges, connections, etc. No estimate of the quantity of fugitive emissions can be made, although high pressures like those found in this section tend to increase the severity of the fugitive emission problem. Any of the materials present in the process streams found in this section could be released as a fugitive emission.

7.2.2 Trace Constituents

The inlet gas stream to the shift reaction section may contain any of the trace elements present in the coal feed to the gas production section. As the gas is cooled in the shift reaction waste heat boiler, some of the trace elements present in the gas may enter the process condensate stream. Similarly, as the gas passes over the shift reactor catalyst, some of the trace elements may become adsorbed/absorbed on the catalyst. Those trace elements not entering the process condensate stream or adhering to the shift reactor catalyst leave the shift reaction section in the gas sent to the gas cooling section. Table 7-2 lists the trace elements found in the condensate streams from one commercial Lurgi coal gasification facility. A

Table 7-2. TRACE ELEMENTS FOUND IN GAS LIQUORS

Element	Concentration, ppm by wt.
Beryllium	0.03-0.06
Boron	3.3
Vanadium	0.3
Manganese	1.0-1.7
Nickel	0.3
Arsenic	1.7-2.3
Cadmium	< 0.03
Antimony	0.1-0.17
Cerium	< 0.1-0.17
Mercury	< 0.03
Lead	0.3-0.6
Bromine	0.3
Fluorine	40
Chlorine	30

Source: Personal communication with EPA

trace element balance for the El Paso coal feed was calculated and given in Tables 4-9, 4-10, 4-11, 5-7 and 5-8.

In addition to the potential for trace elements being picked up by the shift reactor catalyst, sulfur compounds and heavy hydrocarbons may also be adsorbed/absorbed on the catalyst. At this time no information is available as to the types or quantities of trace constituents which may be associated with the spent catalyst.

7.3 CONTROL METHODS

7.3.1 Proven Methods

Shifted Gas. The shifted gas is further processed in other sections to remove the tars, tar oils, phenols, ammonia and sulfur compounds present in this stream. These processing areas provide adequate control for this stream and are discussed in sections 8 and 9.

Process Condensate. The process condensate stream is recycled to the gas production section where it is combined with other condensate streams for use as gasifier effluent quench liquor.

Boiler Blowdown. The blowdown stream from the waste heat boiler is used as makeup water to the plant cooling system. Since the boiler is operating at a relatively low number of cycles of concentration, the dissolved solids content of the blowdown stream is relatively low and does not represent an environmental problem.

Spent Catalyst. The control methods for spent catalyst are not fully developed at this time because of the lack of knowledge about their exact makeup. If the catalyst does not have value sufficient to justify regeneration, the most likely disposal method is as landfill. However, if the catalyst is sufficiently toxic to warrant more elaborate treatment, some of the methods employed for nuclear or hazardous solid waste disposal could be adopted.

Fugitive Emissions. Fugitive air emissions are inevitable in any process which contains fittings, valves, flanges, etc. The high pressures encountered in the shift reaction section tend to increase the likelihood of having fugitive emissions. While fugitive emissions cannot be completely eliminated, the use of best available technology can help to minimize these emissions. Good maintenance practices also help to minimize fugitive emissions.

7.3.2 Potential Methods

The control methods just discussed provide adequate control of the contaminants present in the effluents from the shift reaction section, although many of the control methods are actually other processing areas of the plant. Because of this consideration, effluent control alternatives are not discussed in detail here, but reference is made to the process modification sections of the appropriate other chapters of this report for detailed examination of alternative controls.

7.4 PROCESS MODIFICATIONS

Potential process modifications to the shift reaction section are constrained by the requirements of downstream processing units. It is thus difficult to envision a process modification that would simultaneously fulfill the process requirements and have a significant impact upon the process effluents. The only change that would impact the effluent streams significantly would be a change in the gas composition entering this section.

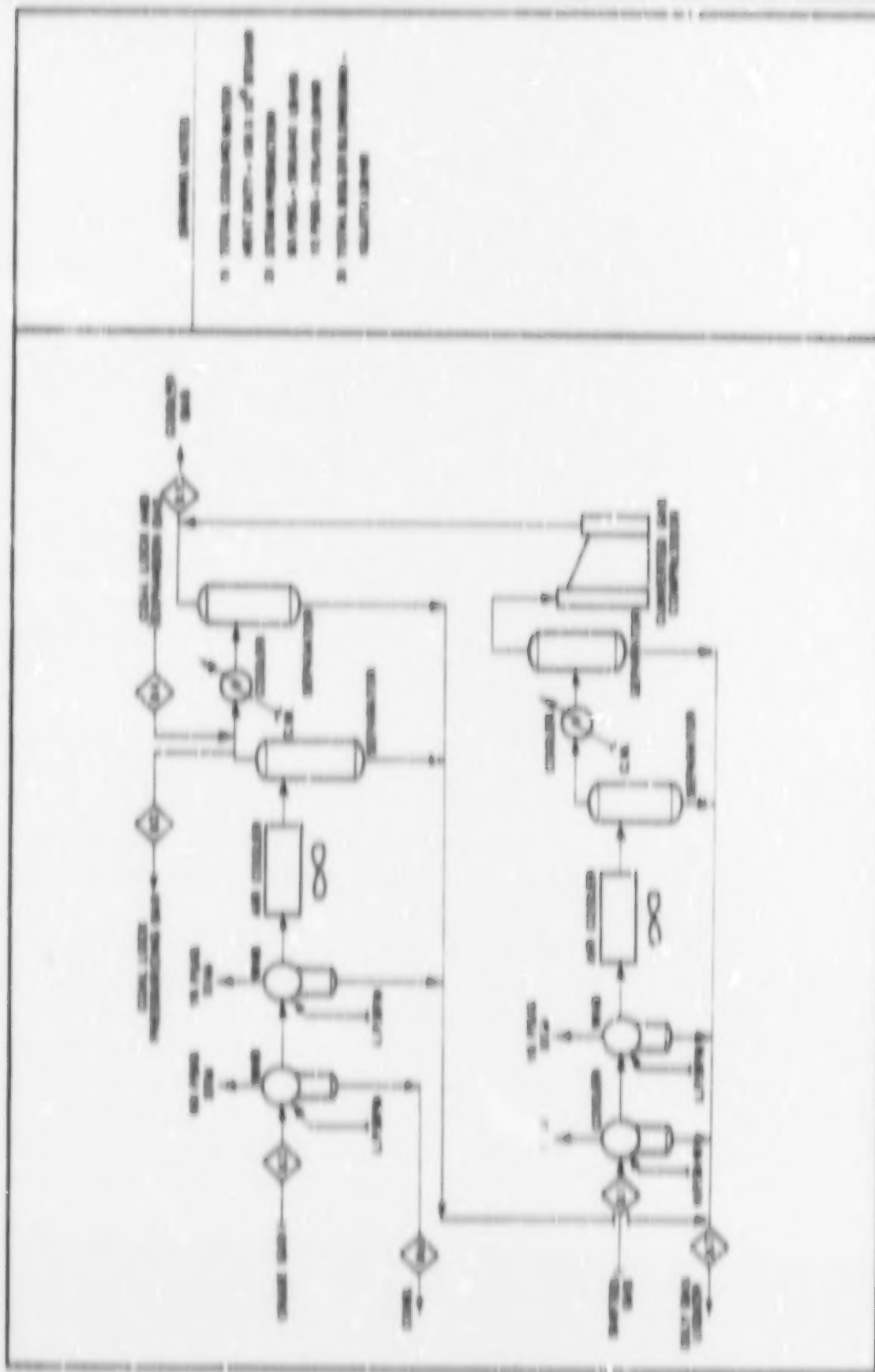
8. GAS COOLING

The gas cooling section of the Lurgi coal gasification process takes shift reactor effluent gas and crude gas from the gas production section and cools them in separate but similar cooling trains. The system of coolers is designed to recover a significant portion of the useful energy content of the gas streams.

8.1 STREAM FLOWS

The process flow scheme and the material balance for the gas cooling section are given in Figure 8-1 and Table 8-1, respectively. The portion of the crude gas from the gas production section that is not directed to the shift reaction section is first cooled in a waste heat boiler that generates 60 psig steam. The condensate from this waste heat boiler is recycled to the gas production section for use as a raw gas quench liquor. The cooled crude gas then undergoes further cooling in a waste heat boiler that produces 15 psig steam, an air cooler and a trim (cooling water) cooler. Upstream of the trim cooler, a portion of the cooled gas is withdrawn and sent to the gas production section for use as coal lock pressurizing gas. Recompressed coal lock gas and expansion gas from the gas purification section are introduced into the raw gas stream after the slipstream draw-off point but prior to the trim cooler. The condensates, or oily gas liquor, formed in the latter three coolers are combined and sent to the by-product recovery section of the plant.

The shift reactor effluent gas is first cooled by exchange with high pressure boiler feed water from the raw water treatment section. The shifted gas then enters, in succession, a waste heat boiler that generates 15 psig steam, an air cooler and a trim (cooling water) cooler. The condensates, or oily gas liquor, formed in all of the above cooling operations are sent to the by-product recovery section. The cooled, shifted gas is next compressed by a steam turbine-driven compressor, combined with the cooled crude gas stream and then sent to the gas purification section.



PROCESS FLOW:

- 1. TOTAL GAS INLET
- 2. TOTAL GAS OUTLET
- 3. TOTAL LIQUID INLET
- 4. TOTAL LIQUID OUTLET
- 5. TOTAL VAPOR INLET
- 6. TOTAL VAPOR OUTLET

Figure 8-1. FLOW SCHEME FOR THE GAS COOLING SECTION

Table B-1. MATERIAL BALANCE FOR THE GAS COOLING SECTION

Stream Number	B.1	B.2	B.3	B.4	B.5	B.6	B.7
Stream Description							
Gas Phase, lb/hr							
Component							
CH ₄	1,298,207	606,262	11,423	26,426	1,692,167	-	-
C ₂ H ₆	95,828	277,222	5,248	22,438	109,402	-	-
C ₃ H ₈	105,512	67,471	1,453	12,462	201,921	-	-
i-C ₄ H ₁₀	7,288	6,123	116	480	13,807	-	-
n-C ₄ H ₁₀	6,710	5,583	104	824	13,103	-	-
C ₅ H ₁₂	10,700	8,962	169	1,312	21,074	-	-
C ₆ H ₁₄	10,700	8,962	169	429	12,215	-	-
n-C ₇ H ₁₆	5,000	5,176	102	3,167	106,514	-	-
H ₂	62,432	20,439	727	585	2,462	-	-
N ₂	357,345	632,286	299	171	20,003	-	-
Argon	10,439	9,066	171	-	-	-	-
CO ₂	15,214	12,483	-	-	-	-	-
Water	3,469	3,353	-	-	-	-	-
Thermal	4,462	4,126	-	-	-	-	-
Oil	6,000	7,469	-	-	-	-	-
Total Gas, lb/hr	1,796,312	1,702,667	20,006	60,711	2,472,606	-	-
Liquid Phase, lb/hr							
Component							
H ₂ O	-	-	-	-	-	20,000	693,470
Tar (oil)	-	-	-	-	-	-	20,000
Tar	-	-	-	-	-	-	7,316
Thermal	-	-	-	-	-	-	9,123
Disassembled (H ₂)	-	-	-	-	-	0,202	77,629
Disassembled (C ₂ H ₆)	-	-	-	-	-	57	47,126
Disassembled (C ₃ H ₈)	-	-	-	-	-	-	-
Disassembled (C ₄ H ₁₀)	-	-	-	-	-	5	16
Disassembled (C ₅ H ₁₂)	-	-	-	-	-	28	26
Disassembled (C ₆ H ₁₄)	-	-	-	-	-	-	-
Disassembled (C ₇ H ₁₆)	-	-	-	-	-	-	-
Total Liquid, lb/hr	-	-	-	-	-	312,992	770,763
Temperature, °F	150	100	180	60	90	300	220
Pressure, psia	400	420	430	430	425	400	385

8.2 POTENTIAL EFFLUENTS

The following sections discuss the potential effluents from the gas cooling section of the Lurgi coal gasification process. The effluent streams include:

- Cooled Gas
- Recycle Process Condensate
- Oily Gas Liquor
- Coal Lock Pressurizing Gas
- Waste Heat Boiler Blowdown
- Fugitive Emissions

The major pollutants in each stream are addressed in Section 8.2.1, while the presence of trace constituents is discussed in Section 8.2.2. For the purpose of this study, trace constituents are assumed to be those components originally entering the gas cooling section in trace quantities.

8.2.1 Major Pollutants

The major pollutants contained in the effluents from the gas cooling section are necessarily restricted to the major pollutants contained in the two major inlet gas streams to the section. These pollutants include:

- Tars
- Tar Oils
- Phenols
- Naphtha
- H_2S
- COS
- NH_3
- CO_2

The other major constituents of the inlet streams are considered to be desirable compounds. The following sections discuss what is known about how these major pollutants distribute themselves in the gas cooling section effluent streams.

Cooled Gas. The cooled gas stream leaving the gas cooling area contains essentially all of the H_2S , CO_2 and naphtha contained in the influent streams to that section. However, during the cooling processes the tars, tar oils, phenols and ammonia present in the inlet streams are removed with the condensed water. Therefore, negligible amounts of these heavier components are present in the cooled gas stream. The anticipated composition of this stream is shown below.

<u>Component</u>	<u>Vol %</u>	<u>Component</u>	<u>Vol %</u>
CO_2	32.2	C_2H_6	0.6
CO	11.7	N_2+Ar	0.3
CH_4	10.7	H_2	43.6
$H_2S + COS$	0.3	H_2O	0.1
C_2H_4	0.4	Naphtha	0.2

Process Condensate. The condensate from the first crude gas waste heat boiler contains dissolved CO_2 , CH_4 , CO and H_2S . In addition, a portion of the heavy hydrocarbons present in the crude gas stream would probably be found in this condensate, although these components are not shown in the material balance given in Table B-1.

Oily Gas Liquor. The condensate streams produced in all of the gas cooling operations, except for that stream generated in the first crude gas waste heat boiler, are combined and directed to the plant by-product recovery section. This condensate, or oily gas liquor, contains essentially all of the tars, tar oils, phenols and ammonia originally present in the cooling section inlet gas. Some CO_2 , H_2 and CH_4 are also present in the oily gas liquor. The percent composition of this liquid stream is shown below.

<u>Component</u>	<u>Wt. %</u>	<u>Component</u>	<u>Wt. %</u>
H ₂ O	86.0	NH ₃	2.3
CO ₂	5.9	Tar Oil	3.6
H ₂	< 0.1	Tar	1.0
CH ₄	< 0.1	Phenol	1.2

Tables B-2 through B-4 give further details on the compounds that constitute the tars, tar oils and phenols.

Table B-2. TAR ANALYSIS

<u>Distillation Range</u>	<u>(1)</u> <u>Percent</u>	<u>(2)</u> <u>Percent</u>
Water	2.1	1.8
0° to 210°C	1.1	1.2
210° to 230°C	1.2	1.6
230° to 270°C	11.1	9.8
270° to 300°C	7.2	6.3
300° to 330°C	27.7	28.6
Residue-Pitch	48.8	50.0
Distillation loss	<u>0.8</u>	<u>0.7</u>
	100.0	100.0
Tar Acids		7.11
Free Carbon		2.16%
Ash		0.16%
Sulfur		0.77%
Specific gravity at 15.8°C	1.126	1.124

Source: (1) Westfield
(2) Westfield

Table 8-3. TAR OIL ANALYSIS

Distillation Range: Percent	(1) °C	(2) °C
5	197.5	182.5
20	207.0	189.5
40	223.0	211.0
60	239.0	235.0
80	277.5	274.0
95	353.5	350.0
Tar Acids		16.5%
Pyridine Bases		1.3%
Sulfur		0.29%
Naphthalene		7.6%
Specific Gravity at 15.5°C	1.005	0.975

Source: (1) Westfield
(2) Westfield

Table 8-4. COMPOSITION OF THE CRUDE PHENOLS

Component	Wt. %
Phenol	59.9
Cresols	20.6
Xylenols	7.6
Catechols	7.3
Resorcinols	4.6
	100.0

Source: Private communication with EPA.

Coal Lock Pressurizing Gas. The temperature of the inlet gas to the trim cooler for the crude gas stream is estimated to be approximately 180°F. At this temperature, only negligible amounts of tars, tar oils, phenols and ammonia remain in the gas phase. Therefore, since the coal lock pressurizing gas is withdrawn from this stream, it too has negligible quantities of these pollutants. However, this stream does contain H₂S, COS, and other organic sulfur compounds since these compounds are still present in the main crude gas stream. The percentage composition of the coal lock pressurizing gas is shown below.

<u>Component</u>	<u>Vol %</u>	<u>Component</u>	<u>Vol %</u>
CO ₂	27.5	C ₂ H ₆	0.6
CO	19.8	N ₂ +Ar	0.3
CH ₄	10.9	H ₂	38.2
H ₂ S + COS	0.4	H ₂ O	1.7
C ₂ H ₂	0.4	Naphtha	0.2

Boiler Blowdown. The waste heat boilers utilized in the gas cooling section use softened water for boiler feed. This inlet stream contains some dissolved solids, consisting mainly of Na⁺, SO₄²⁻, Cl⁻, CO₃²⁻ and silicates. Only very small amounts of Ca⁺⁺ and Mg⁺⁺ are present. To prevent scaling of the boiler tubes, a portion of the boiler water is removed as blowdown. Since the boiler operates at approximately seven cycles of concentration, this blowdown stream contains seven times the inlet concentration of each ionic species. Since no other pollutants are anticipated to be present in the boiler blowdown stream, it is directed to the plant cooling system for use as makeup water.

Fugitive Emissions. Fugitive emissions from the gas cooling section arise from leaks around valves, flanges, connections, etc. No estimate of the quantity of fugitive emissions can be made, although high pressures like those found in this section tend to increase the severity of the fugitive emissions problem. Any of the materials present in the process streams found in this section could be released as a fugitive emission.

8.2.2 Trace Constituents

The inlet gases to the gas cooling section may contain any of the trace elements present in the coal feed to the gasification section (see Chapter 4). Prediction of the fate of these trace elements is complicated by a lack of knowledge regarding the chemical form in which they exist, i.e., as oxides, hydrides, sulfides, etc. It is anticipated that as the gases are cooled, certain trace elements will be removed from the gas phase. Some of the more volatile trace elements such as mercury, bromine, chlorine, fluorine, selenium and tellurium may be retained in the gas phase. Less volatile trace elements might have a higher likelihood of being found in the condensates produced during the cooling operations. Exact quantification of the trace element distribution in the effluent streams from the gas cooling section cannot be made at this time, however. Trace elements found in the condensate streams from one commercial Lurgi coal gasification facility were given in Table 7-2, Chapter 7. Trace element balances for the El Paso coal feed composition were calculated and given in Tables 4-9, 4-10, and 4-11, Chapter 4, and Tables 5-7 and 5-8, Chapter 5.

8.3 CONTROL METHODS

The gas cooling section does not discharge any effluent stream, with the exception of fugitive emissions, directly to the environment. Instead, these streams are directed to other processing areas for treatment or reuse. In this section the destination of each process effluent from the gas cooling section is identified.

8.3.1 Proven Methods

Cooled Gas. The main effluent gas stream from the gas cooling section is sent to the gas purification section for removal of acid gases, naphtha and water. Since the rest of the major components of this stream are considered

to be desirable gases, the gas purification section represents an adequate control for the cooled gas stream.

Process Condensate. The condensate from the first crude gas waste heat boiler is directed to the gas production section where it is combined with other condensate streams for use as raw gas quench liquor.

Oily Gas Liquor. The contaminated condensates generated during the cooling operations in this section (with the exception of the process condensate stream discussed above) are sent directly to the by-product recovery section for removal and recovery of tars, tar oils, phenols, ammonia and dissolved gases. These treatment operations are discussed in detail in Section 11.

Coal Lock Pressurizing Gas. A slipstream from the crude gas cooling train is used to pressurize the coal locks in the gas production area. Since this stream contains sulfur compounds and naphtha, provisions must be made in the gas production area to contain and recycle essentially all of the lock gas. Section 6 discusses in detail the operation of the coal locks and the emissions resulting from their use.

Boiler Blowdown. The blowdown streams from the waste heat boilers are collected and used as makeup water to the plant cooling system. Since the boilers are operating at a relatively low number of cycles of concentration, the dissolved solids content of these blowdown streams is relatively low and does not represent an environmental problem.

Fugitive Emissions. Fugitive air emissions are inevitable in any process which contains fittings, valves, flanges, etc. The high pressures encountered in the gas cooling section tend to increase the likelihood of having fugitive emissions. While fugitive emissions cannot be completely eliminated, the use of best-available technology such as mechanical seals on pumps can help to minimize these emissions. Good maintenance practices also help to minimize fugitive emissions.

8.3.2 Potential Methods

The control methods just discussed provide adequate control of the contaminants present in the effluents from the gas cooling section, although many of the control methods are actually other processing areas of the plant. Because of this consideration, effluent control alternatives are not discussed in detail here, but reference is made to the process modification sections of other appropriate chapters of this report for detailed examination of alternative controls.

8.4 PROCESS MODIFICATIONS

Potential process modifications to the gas cooling section are constrained by the requirements of downstream processing units. It is thus difficult to envision a process modification that would simultaneously fulfill the process requirements and have a significant impact upon the process effluents. The only change that would impact the effluent streams significantly would be a change in the gas composition entering this section.

9. GAS PURIFICATION

In the gas purification section the Rectisol I process is used to remove acid gases such as CO_2 , H_2S , COS , CS_2 , mercaptans, etc., from inlet gas streams by physical absorption of these acid gases in a methanol solvent. Rectisol I, which does not selectively absorb H_2S from gases containing CO_2 , is commercially available and has been proven to be a reliable acid gas cleanup process.

As is the case with all acid gas cleanup processes based upon physical absorption, the Rectisol I process operates more efficiently at high pressures (up to 1000 psi). This effect is due to the fact that the solubility of the acid gases in methanol increases with increasing pressure. Low temperatures ($<0^\circ\text{F}$) also increase the solubility of the acid gases in methanol.

The solubility coefficients of various gases in methanol as a function of temperature are presented in Figure 9-1. These coefficients are a measure of the ratio of the amount of gas found in the liquid phase to the amount of gas found in the vapor phase at equilibrium and a gas partial pressure of 1 atm. These coefficients generally increase with increasing partial pressure. The influence of partial pressure, which becomes minimal at high temperatures, is most significant when the dew point of the gas is approached. Figure 9-1 shows that the solubilities of the gases which are usually considered to be impurities (H_2S , COS , and CO_2) increase with decreasing temperatures. It should also be noted that the solubilities of gases which are normally considered to be valuable products (CO , CH_4 , and H_2) are not significantly affected by temperature. This indicates that the Rectisol process is more efficiently operated at low temperatures, a condition which also minimizes the solvent losses.

Disadvantages associated with the Rectisol process include: (a) the methanol solvent retains heavy hydrocarbons (C_{10}) which must be removed; (b) since the process operates at low temperatures (0°C), a significant refrigeration load is required; and (c) there is a potential for high solvent losses due to the volatility of methanol.

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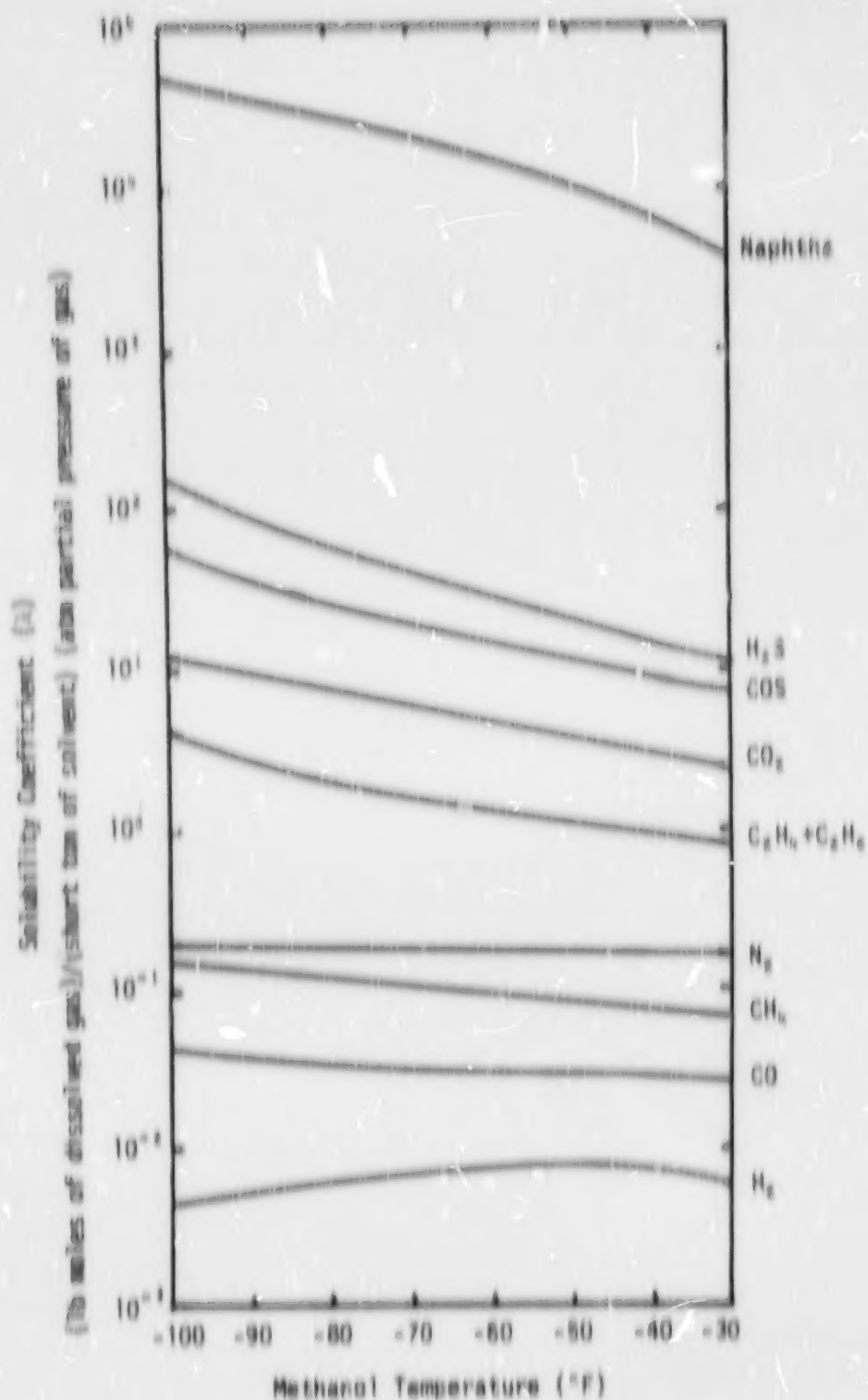


Figure 9-1: SOLUBILITY OF GASES IN METHANOL.

Source: Schulz, Walter H. Rectisol: A low-Temperature Scrubbing Process for Gas Purification, *Advan. Chem. Eng. 15*, 406, 14 (1974).

9.1 STREAM FLOWS

The process flow scheme and the material balance for the Rectisol I acid gas removal process are given in Figure 9-2 and Table 9-1, respectively. The mixed gas from the gas cooling section is cooled by refrigeration to 32°F before entering the prewash column. The column operates at the pressure of the feed gas, approximately 425 psia. In the prewash column a stream of CO_2 - and H_2S -rich methanol from the main absorber is used to remove water, naphtha and residual heavy hydrocarbons and ammonia from the cooled product gas stream. The prewashed gas leaving the top of the absorber is further cooled to about -50°F before entering the main absorber.

The methanol from the prewash column enters the prewash flash tank where most of the CO_2 , H_2 , H_2S , COS , organic sulfur, and lighter hydrocarbons are flashed off. The flashed methanol is sent to the naphtha separator where water is used to extract the methanol from the naphthas and any heavier hydrocarbons. The naphtha is recovered as a by-product while the methanol/water mixture is sent to the methanol/water still where the methanol and the gases in solution are separated from the water by distillation. The water, or process condensate, is sent to the plant water treatment system while the methanol vapor and acid gases are fed to the hot regenerator.

The main absorber operates at 425 psia and -50°F. The prewashed gas countercurrently contacts a pure methanol stream from the hot regenerator, resulting in the removal of acid gas components including H_2S , COS , CO_2 , and organic sulfur compounds. As mentioned earlier, a small slipstream from this absorber is sent to the prewash column. The rich absorber effluent stream is then sent to the flash regenerator.

In the flash regenerator column the solvent passes through a series of pressure reduction stages. In the first stage the pressure is reduced enough to flash off primarily the desired product gases, i.e., CO , H_2 , and CH_4 . This flash, or expansion gas, is recycled to the gas cooling section. In the following stages the pressure is reduced to atmospheric or subatmospheric levels to

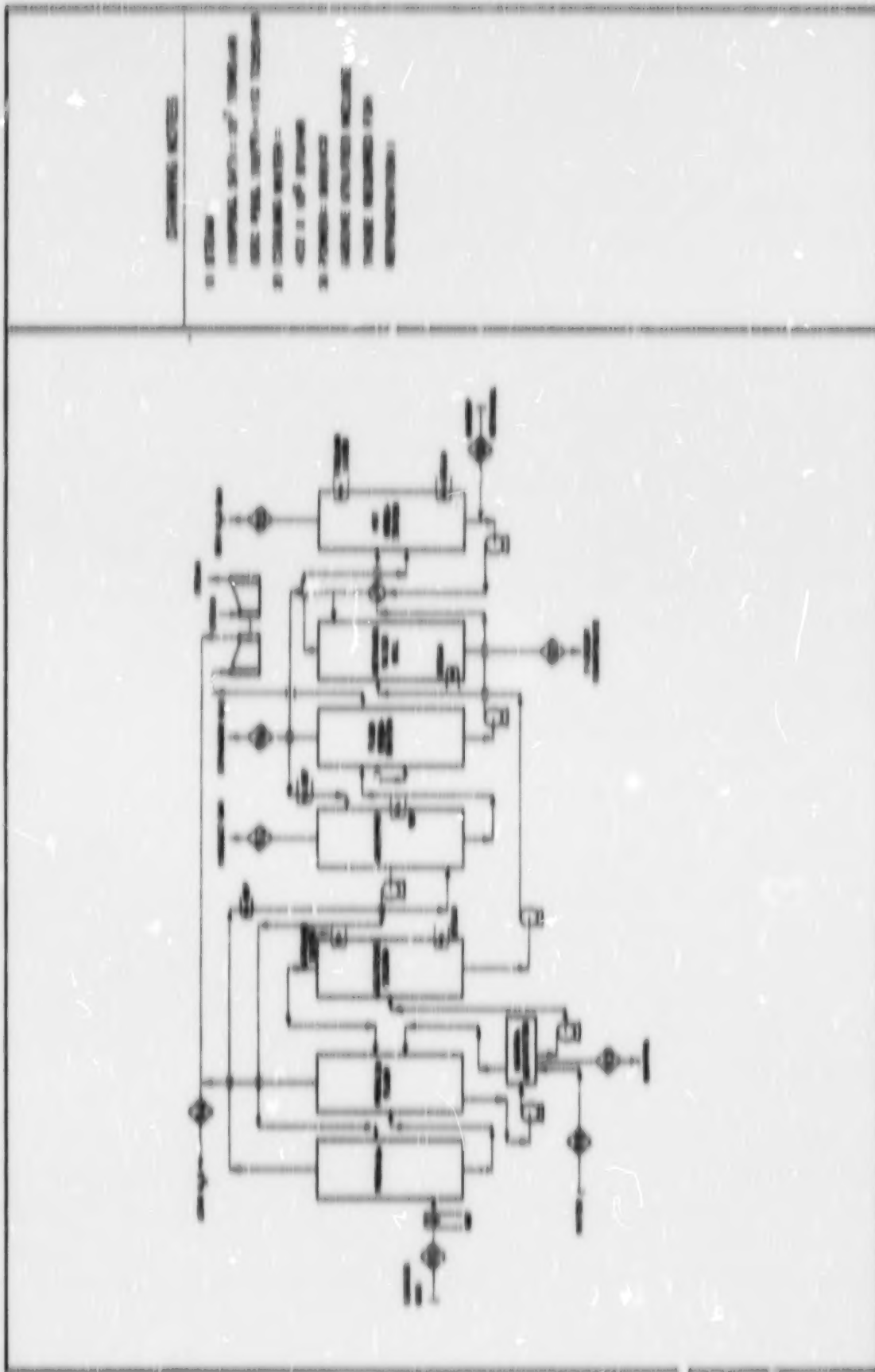


Figure 9-2. FLOW SCHEME FOR THE GAS PURIFICATION SECTION - REVERSAL PROCESS

Table 9-1. MATERIAL BALANCE FOR THE GAS PURIFICATION SECTION - DISTILLATE 1 PROCESS

Stream Number	9.1	9.2	9.3	9.4	9.5	9.6	9.7	9.8	9.9
Stream Description	Wet Gas From Gas Cooling	Product Gas	By-Product Naphtha	Lean H ₂ S Acid Gas	Rich H ₂ S Acid Gas	Regeneration Gas	Process Naphtha	Stripper Naphtha	Bottoms to Naphtha Distillation
Component									
Gas Phase, Bbl/hr									
Hydro	1,682,367	110,317	-	1,538,329	31,689	17,376	-	-	-
H ₂ S	11,462	-	-	9,617	4,385	-	-	-	-
C ₂ H ₆	17,103	10,175	-	2,388	-	578	-	-	-
C ₃ H ₈	388,453	383,301	-	1,729	-	4,582	-	-	-
i-C ₄ H ₁₀	156,516	167,515	-	316	-	689	-	-	-
n-C ₄ H ₁₀	203,821	193,296	-	3,389	-	1,366	-	-	-
i-C ₅ H ₁₂	21,079	16,363	-	3,382	3	976	-	-	-
n-C ₅ H ₁₂	12,276	12,387	-	-	2,680	108	-	-	-
Total Dry Gas, Bbl/hr	2,658,888	659,706	-	1,558,367	68,367	31,416	-	-	-
Liquid Phase, Bbl/hr									
Component									
H ₂ S	2,485	-	-	-	-	-	187,483	-	188,368
Naphtha	26,175	-	28,683	-	-	-	-	2,680	-
Refluxant	-	-	-	-	-	-	-	-	-
Total Liquid, Bbl/hr	27,660	-	28,683	-	-	-	187,483	2,680	188,368
Temperature, °F	25	-50	32	-50	80	-50	120	80	240
Pressure, psia	625	625	16.7	25	16.7	160	16.7	16.7	16.7

drive off the bulk of the CO_2 along with lesser amounts of H_2S and COS . These gases are combined with the prewash flash gas to form a lean H_2 gas stream which is sent to the sulfur recovery section.

The flash-regenerated methanol stream is then pumped to the hot regenerator where it is combined with the methanol/water still over and product. In the hot regenerator the sorbed acid gases are stripped from the methanol. The top of this column is cooled using either cooling water or a refrigerant. A low column overhead temperature is desirable here since this minimizes methanol losses. The uncondensed gases, which are rich in H_2S , are sent to the sulfur recovery section. The regenerated methanol is cooled and returned to the main absorber.

9.2 POTENTIAL EFFLUENTS

9.2.1 Major Pollutants

Lean H_2S Flash Gas. The gas streams generated in the prewash flash and in the main flash regenerators are comprised primarily of CO_2 (~98% by volume), with smaller amounts of CO , H_2 , CH_4 , C_2H_4 , C_2H_6 , H_2S , and COS . The amounts of these compounds present depend upon the composition of the raw gas from the gasifier and the operating parameters of the Rectisol I process such as absorber temperature and pressure. The flash gas composition is shown below.

<u>Component</u>	<u>Vol %</u>	<u>Component</u>	<u>Vol %</u>
CO_2	97.5	H_2	0.4
H_2S	0.8	CH_4	0.6
C_2H_6	0.2	C_2H_4	0.3
CO	0.2	N_2+Ar	trace

The presence of sulfur compounds necessitates further treatment of this stream. The method of treatment depends upon several factors, including the amounts and types of sulfur compounds present.

Rich H₂S Gas. The off-gases from the hot regenerator are comprised primarily of CO₂, CO, H₂, CH₄, H₂S, and COS. The concentration of H₂S is higher in this stream (~13% by volume) than in the flash gases. The concentrations of the other components depend primarily upon operating parameters such as the flash regeneration pressure. This stream may also contain substantial amounts of methanol, depending upon the product gas (overhead) temperature and the pressure of the hot regenerator. The effect of temperature and pressure on the methanol concentration in the off-gas is shown in Figure 3-3. For example, operating the hot regenerator with an overhead temperature of 1 atm and -40°F would result in a methanol mole fraction in the off-gas of 0.001. Increasing the overhead temperature to 100°F would result in a methanol mole fraction of 0.32. Increasing the regenerator pressure to 20 atmospheres would reduce the methanol mole fraction in the off-gas to 0.00005 at -40°F and 0.0165 at 100°F. A typical gas composition is shown below.

<u>Component</u>	<u>Vol %</u>	<u>Component</u>	<u>Vol %</u>
CO ₂	78.8	H ₂	trace
H ₂ S	12.6	CH ₄	trace
C ₂ H ₆	trace	C ₃ H ₈	trace
CO	trace	N ₂ +Ar	trace
		Methanol	8.6

This gas stream is sent to the sulfur recovery section.

Expansion Gas. The gases released during the first stage of flash regeneration are comprised of CO₂, CO, CH₄, C₂H₆, C₃H₈, H₂, and some N₂+Ar. The amount of each component present depends upon the flash pressure and the concentration of the component in the methanol stream fed to the flash regenerator. The composition of this gas stream is shown below.

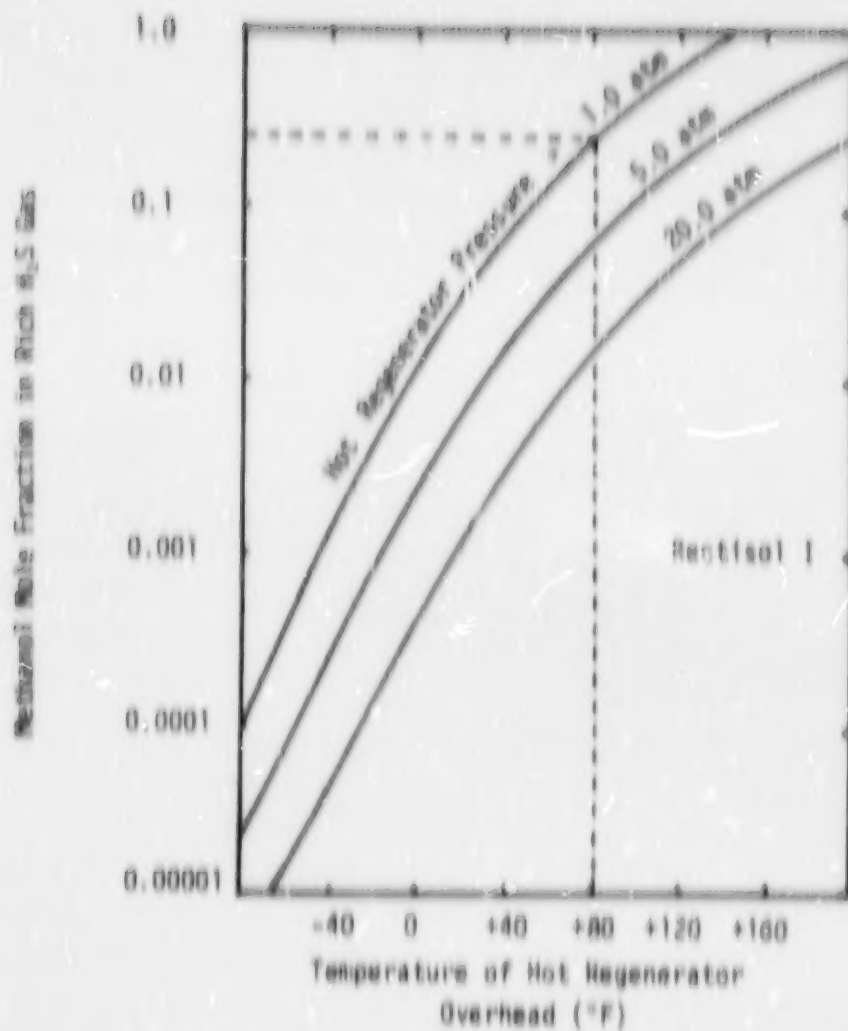


Figure 9-3. EFFECT OF OVERHEAD TEMPERATURE AND PRESSURE OF HOT REGENERATOR ON METHANOL MOLE FRACTION IN RICH H_2S GAS

<u>Component</u>	<u>Vol. %</u>	<u>Component</u>	<u>Vol. %</u>
CO ₂	31.1	H ₂	18.6
H ₂ S	trace	CH ₄	33.4
C ₂ H ₆	1.6	C ₃ H ₈	2.4
CO	12.6	N ₂ +Ar	0.3

Since this stream contains such high concentrations of desirable gases, it is recombined with the cooling section product gas upstream of the acid gas removal section.

Product Gas. The product gas exiting the Rectisol process is comprised of CO, H₂, CH₄, C₂H₆, C₃H₈ and, depending upon the required product specifications, possibly small amounts of CO₂, H₂S, COS and organic sulfur. The product gas composition is shown below.

<u>Component</u>	<u>Vol. %</u>	<u>Component</u>	<u>Vol. %</u>
CO ₂	3.1	H ₂	63.5
H ₂ S	trace	CH ₄	14.9
C ₂ H ₆	0.5	C ₃ H ₈	0.7
CO	16.9	N ₂ +Ar	0.4

This gas stream is sent to the methanation section for conversion into substitute natural gas (SNG).

By-Product Naphtha. The by-product naphtha stream consists of C₆-C₁₀ (predominantly aromatic) hydrocarbons removed in the prewash. Some of the expected compounds present in the by-product naphtha stream are listed below.

Major Components (-10% each)

Paraffins and Olefins
Benzene
Toluene
Xylenes + Ethyl Benzene
Trimethyl Benzenes

Minor Components (-10% each)

Thiophenes
Styrene
Ethyl Toluene
Indane
Indene
Naphthalene
Benzofuran

Source: Private communications with EPA.

This stream, which may also contain small amounts of dissolved acid gases, ammonia, and phenols, is sent to a by-product storage facility.

Process Condensate. The process condensate from the methanol/water still is comprised primarily of the water in the feed gas and the water used in the naphtha extraction operation. It may contain small amounts of phenol, cyanide, ammonia, sulfides, and hydrocarbons such as naphthas and methanol. The process condensate stream composition is given below.

<u>Component</u>	<u>ppm (weight)</u>
Phenol	18
Cyanide (as CN)	10.4 (includes thiocyanate)
Ammonia (as N)	42
Sulfides (as S)	trace

Source: Private communications with EPA.

This stream is sent to the wastewater treatment section.

Fugitive Emissions. Fugitive air emissions from the Rectisol I acid gas removal process arise from leaks around pump seals, valves, flanges, etc. High pressures like those encountered in this process enhance fugitive leaks from equipment. The compositions of these fugitive emissions would be a mixture of any of the various components found in the process streams.

9.2.2 Trace Constituents

There is the possibility of trace element contamination of all the effluent streams discussed in Section 9.2.1. Any of the trace elements found in the coal feed to the gasifier may be present in the raw gas. However, during the gas cooling operation many of the less volatile trace elements may be removed from the gas stream. Trace elements which may be present in coal are shown below.

Be	Mn	As	Sb	Pb	Se
B	Ni	F	Ce	Br	Te
V	As	Cd	Hg	Cl	

The more volatile elements, including mercury, bromine, chlorine, fluorine, selenium, and tellurium, may reach the gas purification area. The fate of these trace elements is not known; however, they may be present to some extent in all the effluent streams from this process.

9.3 CONTROL METHODS

9.3.1 Proven Methods

Stratford Process. The Stratford process is a proven, commercially available process for the recovery of elemental sulfur from gas streams containing H_2S . It is capable of removing H_2S to a level of 1 ppmv. This process does not remove other acid gas components such as CO_2 and CS_2 in a regenerable manner. In order to remove these compounds, they must first be converted to H_2S by a catalytic conversion process such as the Carpenter-Evans or Holmes-Maxted processes.

Claus Process. The Claus process is a commercially available process for the recovery of sulfur from gas streams containing H_2S . To be economically feasible, this process requires a concentration of approximately 10 to 15% by volume of H_2S . The overall sulfur recovery efficiency of the Claus process is

typically 95 percent, with some organic sulfur being formed and/or destroyed, depending upon the system's operating conditions and the feed gas composition.

Wastewater Treatment. The process condensate stream can be treated to remove dissolved organics and/or inorganics by any of several commercial processes. Since the stream is directed to the wastewater treatment areas of the plant, the available control methods will be discussed in Section 14.

9.3.2 Potential Control Methods

Potential methods are considered to be those requiring some process development before they can be utilized in a plant design. Adequate control can be achieved with the methods discussed, or with alternate methods discussed in Section 9.4.

9.4 PROCESS MODIFICATIONS

9.4.1 Alternative Acid Gas Removal Processes

There are many commercially available acid gas removal processes which can perform the same function as the Rectisol I process. Table 9-2 lists most of these by type of process. Each of these processes has different advantages and limitations which must be considered for each application.

9.4.2 Rectisol II

While the Rectisol I process can reduce the acid gas concentration of the synthesis gas to the level dictated by the methanation operation, it may be desirable to remove the sulfur compounds and CO₂ selectively to either increase the percentage recovery of the sulfur compounds or to improve the economics of the sulfur recovery operation. There are many processes which may be operated selectively, including the Purisol, Selexol, and Rectisol II processes. The latter, which is a modification of the Rectisol I process, is discussed

TABLE 9-2. COMMERCIALY AVAILABLE ACID GAS REMOVAL PROCESSES

Physical Solvent Processes

Rectisol

Purisol

Estasolvan

Fluor Solvent

Selexol

Direct Conversion

Manchester

Perox

Fixed-Bed Adsorption

Haines

Molecular Sieve

Chemical Solvent

MEA

DEA

MDEA

DIPA

DGA

Glycol + Amine

Benfield

Catacarb

Catalytic Conversion

Holmes-Maxted

Carpenter-Evans

Chemical/Physical Solvent

Amisol

Sulfinol

in the following paragraphs. A process flow scheme and a material balance for a typical Rectisol II process are shown in Figure 9-4 and Table 9-3, respectively.

The Rectisol II process is identical to the Rectisol I process with respect to the prewash section. The major difference is in the main absorber. The absorber used in the Rectisol II process is composed of three sections. In the bottom section the prewashed gas is contacted with CO₂-rich methanol from the upper sections, resulting in the removal of sulfur compounds such as H₂S, COS and CS₂. The desulfurized gas then enters the second stage where it is contacted with flash-regenerated methanol to achieve bulk CO₂ removal. The gas then enters the third stage where it contacts hot regenerated methanol for final cleanup to meet product gas specifications with respect to H₂S and CO₂.

The third-stage methanol stream is combined with that from the second stage, resulting in essentially a CO₂ saturated methanol stream. The majority of this stream is sent to the bulk CO₂ flash regenerator with smaller streams feeding the prewash column and the desulfurization section. In the bulk CO₂ flash regenerator most of the CO₂ is flashed off by pressure reduction. The resulting CO₂-lean methanol stream is then recycled to the second stage of the main absorber. The effluents from this process are discussed below.

Lean H₂S Flash Gas. The gas streams generated in the prewash flash and in the main flash regenerators are comprised primarily of CO₂ (~96% by volume), with smaller amounts of CO, H₂, CH₄, C₂H₄, C₂H₆, H₂S, and COS. The amounts of each of these compounds which are present depend upon the composition of the raw gas from the gasifier and the operating parameters of the process such as absorber temperature and pressure. The flash gas composition for this modification is shown below.

<u>Component</u>	<u>Vol %</u>	<u>Component</u>	<u>Vol %</u>
CO ₂	96.6	CO	0.4
H ₂ S + COS	1.3	H ₂	0.3
		CH ₄	0.7
C ₂ H ₄ + C ₂ H ₆	0.8	N ₂ +Ar	trace

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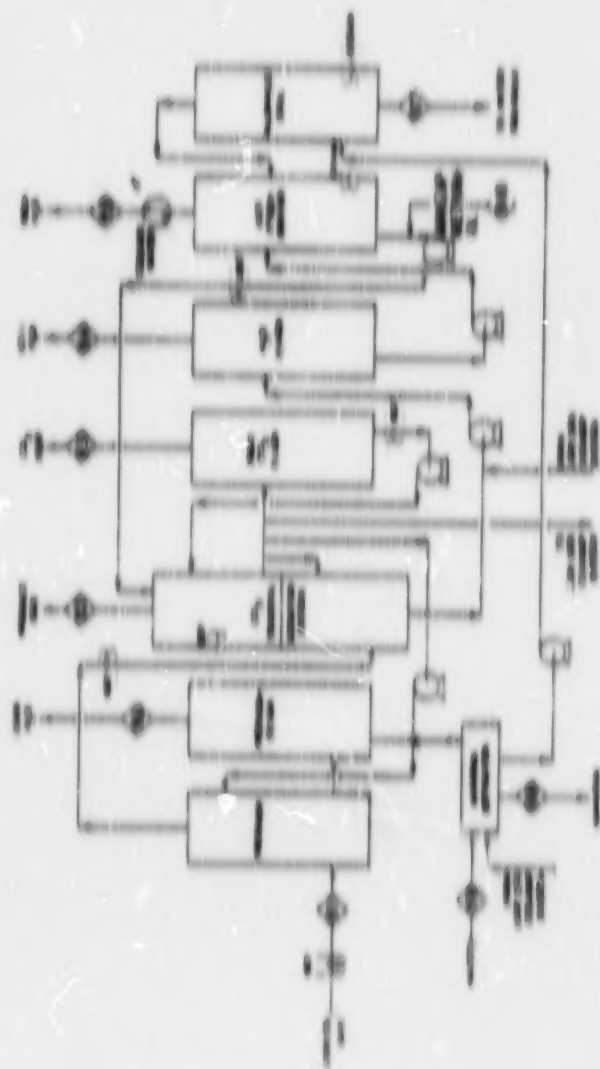


Figure 9-4. FILM SCHEME FOR THE GAS PURIFICATION SECTION - REACTION III PROCESS

Table 9-3. Estimated balance for the gas production system - natural gas production

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The presence of sulfur compounds necessitates further treatment of this stream. The method of treatment depends upon several factors, including the amounts and types of sulfur compounds present.

Rich H₂S Gas. The off-gases from the hot regenerator are comprised primarily of CO₂, CO, H₂, CH₄, H₂S, COS, and organic sulfur. The concentration of H₂S is higher in this stream (~14% by volume) than in the flash gases. This stream may also contain substantial amounts of methanol, as discussed in Section 9.2.1 under Rich H₂S Gas for the Rectisol I process. The rich H₂S gas composition is shown below.

<u>Component</u>	<u>Vol %</u>	<u>Component</u>	<u>Vol %</u>
CO ₂	77.5	CO	trace
H ₂ S + COS	14.0	H ₂	trace
		CH ₄	trace
C ₂ H ₆ + C ₃ H ₈	0.2	N ₂ +Ar	trace
		Methanol	6.6

Bulk CO₂ Flash Gas. The gas stream from the bulk CO₂ flash regenerator is comprised primarily of CO₂ with small amounts of H₂, CO, and hydrocarbons. There should be only trace amounts of sulfur compounds in this stream. A typical bulk CO₂ flash gas composition for the Rectisol II process is given below.

<u>Component</u>	<u>Vol %</u>	<u>Component</u>	<u>Vol %</u>
CO ₂	96.9	CO	0.6
H ₂ S + COS	trace	H ₂	0.6
		CH ₄	1.4
C ₂ H ₆ + C ₃ H ₈	1.4	N ₂ +Ar	0.1

Product Gas. The product gas exiting the Rectisol process is comprised of CO, H₂, CH₄, C₂H₆, C₃H₈ and, depending upon the required product specifications, possibly small amounts of CO₂, H₂S, COS, and organic sulfur. A typical product gas composition is shown below.

<u>Component</u>	<u>Vol %</u>	<u>Component</u>	<u>Vol %</u>
CO ₂	trace	CO	17.4
H ₂ S	trace	H ₂	66.7
COS	trace	CH ₄	15.6
C ₂ H ₆ +C ₃ H ₈	0.9	N ₂ +Ar	0.4

By-Product Naphtha. The by-product naphtha stream consists of C₅-C₈ (primarily aromatic) hydrocarbons removed in the prewash. Some of the expected compounds present in the by-product naphtha stream are listed below.

<u>Major Components (>10% each)</u>	<u>Minor Components (<10% each)</u>
Paraffins and Olefins	Thiophenes
Benzene	Styrene
Toluene	Ethyl Toluene
Xylenes + Ethyl Benzene	Indane
Trimethyl Benzenes	Indene
	Naphthalene
	Benzofuran

Source: Private communications with EPA.

This stream, which may also contain small amounts of dissolved acid gases, ammonia, and phenols, is sent to a by-product storage facility.

Process Condensate. The process condensate from the methanol/water still is comprised primarily of the water in the feed gas and the water used in the naphtha separation operation. It may contain small amounts of phenol, cyanide,

ammonia, sulfides, and hydrocarbons such as naphtha and methanol. A typical process condensate stream composition is given below.

<u>Component</u>	<u>ppm (weight)</u>
Phenol	18
Cyanide (as CN)	10.4 (includes thiocyanide)
Ammonia (as N)	42
Sulfides (as S)	trace

Source: Private communications with EPA.

This stream is sent to the wastewater treatment section.

Fugitive Emissions. Fugitive air emissions from the Rectisol II acid gas removal process arise from leaks around pump seals, valves, flanges, etc. High pressures like those encountered in this process enhance fugitive leaks from equipment. The compositions of these fugitive emissions could be a mixture of any of the various components found in the process streams.

Trace Constituents. There is the possibility of trace element contamination of all the effluent streams discussed in Section 9.4.2. Any of the trace elements found in the coal feed to the gasifier may be present in the raw gas. However, during the gas cooling operation many of the less volatile trace elements may be removed from the gas stream. Trace elements which may be present in coal are shown below.

Be	Hn	As	Sb	Pb	Se
B	Ni	F	Ce	Br	Te
V	As	Cd	Hg	Cl	

The more volatile elements, including mercury, bromine, chlorine, fluorine, selenium, and tellurium, may reach the gas purification area. The fate of these trace elements is not known; however, they may be present to some extent in all of the effluent streams from this process.

10. METHANATION

In the methanation section low BTU synthesis gas is converted to methane rich high BTU gas by the catalyzed reaction of CO, CO₂, and H₂ according to equations 10-1 and 10-2.



Water produced in the methanation section is removed in two stages, condensation and absorption with glycol. The product gas formed will have a heating value of about 980 BTU/scf and will be at a pressure suitable for typical pipeline transport.

10.1 STREAM FLOWS

The process flow scheme for the methanation section is shown in Figures 10-1 and 10-2. The material balance for this area is given in Table 10-1. Product gas from the gas purification section is heated by exchange with previously methanated gas and is fed to the recycle reactor. Here the gas, in contact with pelletized nickel catalyst, undergoes the methanation reactions shown by equations 10-1 and 10-2. The methanated gas is then cooled in a waste heat boiler that will generate 600 psi steam. A portion of this gas is recycled to provide an optimum feed gas temperature, and the rest is sent to a second methanation reactor. This reactor is similar to the recycle reactor, and is used to clean up any unreacted CO, CO₂ and H₂.

Water from the methanation reaction is condensed and separated from the gas stream in several stages. This water is sent to the water treatment section and is eventually used as soft water within the plant. Cooled gas is

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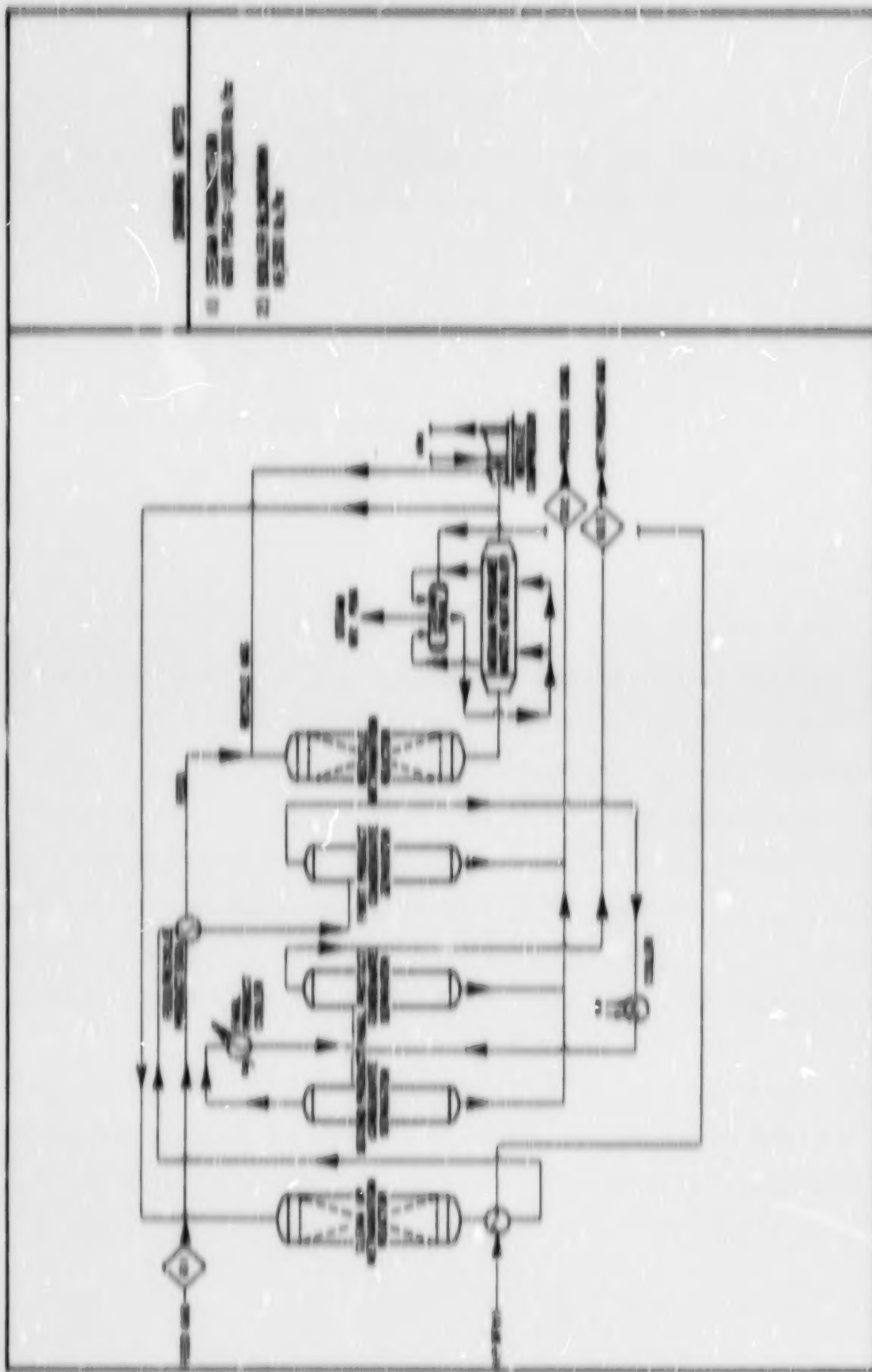


Figure 10-1. FLOW SCHEME FOR THE METHANATION SECTION

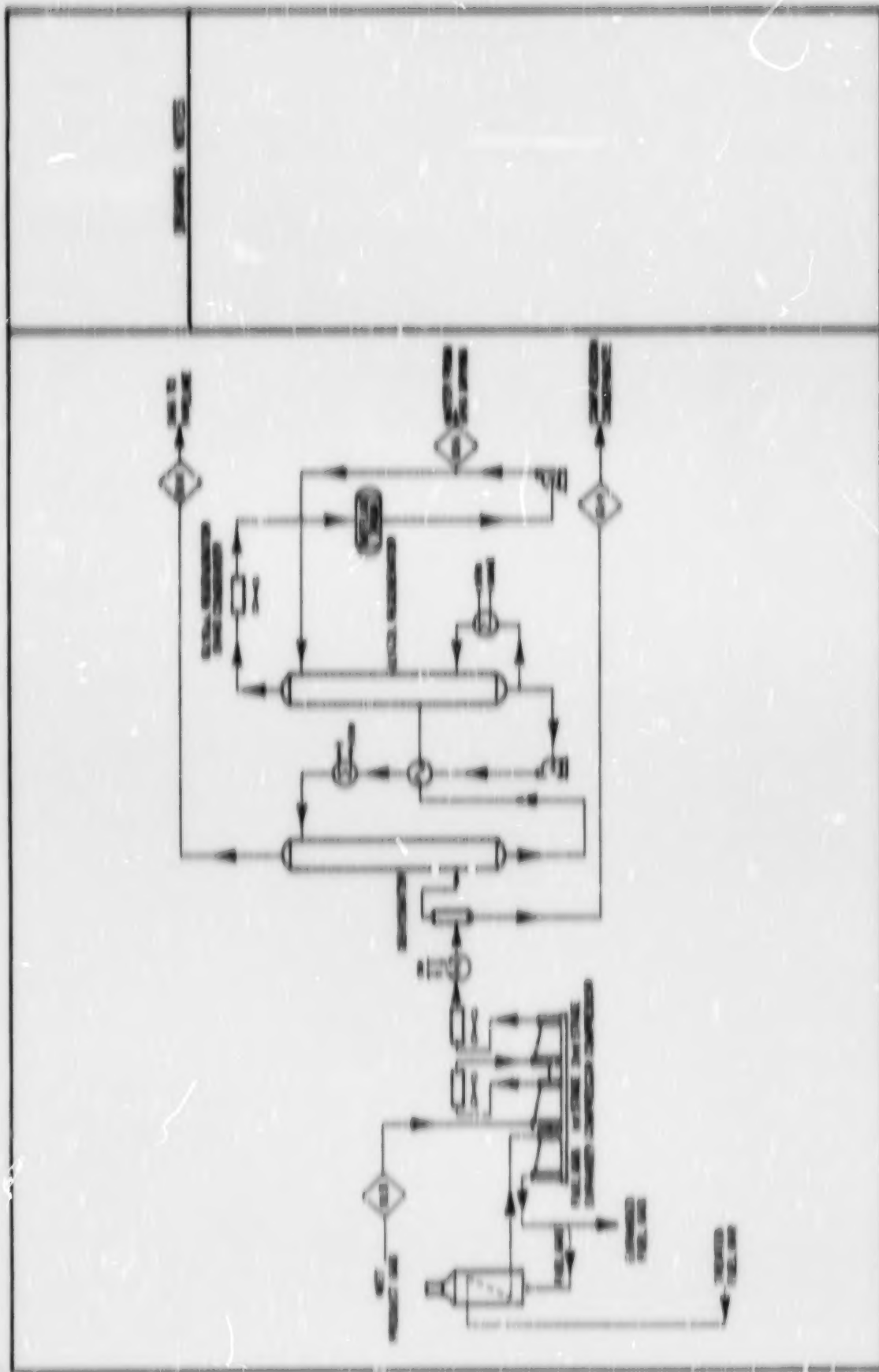


Figure 10-2. FLOW SCHEME FOR THE COMPRESSION AND REGENERATION SECTION

Table 10-5. MATERIAL BALANCE FOR THE METAMATION SECTION

Stream Header		10.1	10.2	10.3	10.4	10.5	10.6
Stream Description		Feed Gas	Process Condensate	Unit Product Gas	Compression Condensate	Water From LNG Drying	Pigging Air
Gas Phase, lb/hr							
Component	Molecular Wt.						
CO ₂	44.010	110.937	00	25.310	00	00	20.310
H ₂	2.016	0.08	00	00	00	00	00
H ₂ O	18.015	10.138	00	00	00	00	00
CH ₄	16.043	281.101	00	00	00	00	00
C ₂ H ₆	30.070	103.613	00	00	00	00	00
C ₃ H ₈	44.095	137.833	00	00	00	00	00
C ₄ H ₁₀	58.122	16.730	00	00	00	00	00
C ₅ H ₁₂	72.150	10.107	00	00	00	00	00
N ₂ + Ar	28.013	00	00	00	00	00	00
H ₂ O	18.015	00	00	00	00	00	00
CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
C ₃ H ₈	44.095	00	00	00	00	00	00
C ₄ H ₁₀	58.122	00	00	00	00	00	00
C ₅ H ₁₂	72.150	00	00	00	00	00	00
N ₂ + Ar	28.013	00	00	00	00	00	00
H ₂ O	18.015	00	00	00	00	00	00
CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
C ₃ H ₈	44.095	00	00	00	00	00	00
C ₄ H ₁₀	58.122	00	00	00	00	00	00
C ₅ H ₁₂	72.150	00	00	00	00	00	00
N ₂ + Ar	28.013	00	00	00	00	00	00
H ₂ O	18.015	00	00	00	00	00	00
CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
C ₃ H ₈	44.095	00	00	00	00	00	00
C ₄ H ₁₀	58.122	00	00	00	00	00	00
C ₅ H ₁₂	72.150	00	00	00	00	00	00
N ₂ + Ar	28.013	00	00	00	00	00	00
H ₂ O	18.015	00	00	00	00	00	00
CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
C ₃ H ₈	44.095	00	00	00	00	00	00
C ₄ H ₁₀	58.122	00	00	00	00	00	00
C ₅ H ₁₂	72.150	00	00	00	00	00	00
N ₂ + Ar	28.013	00	00	00	00	00	00
H ₂ O	18.015	00	00	00	00	00	00
CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
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C ₄ H ₁₀	58.122	00	00	00	00	00	00
C ₅ H ₁₂	72.150	00	00	00	00	00	00
N ₂ + Ar	28.013	00	00	00	00	00	00
H ₂ O	18.015	00	00	00	00	00	00
CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
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C ₄ H ₁₀	58.122	00	00	00	00	00	00
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N ₂ + Ar	28.013	00	00	00	00	00	00
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CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
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C ₂ H ₆	30.070	00	00	00	00	00	00
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CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
C ₃ H ₈	44.095	00	00	00	00	00	00
C ₄ H ₁₀	58.122	00	00	00	00	00	00
C ₅ H ₁₂	72.150	00	00	00	00	00	00
N ₂ + Ar	28.013	00	00	00	00	00	00
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CO ₂	44.010	00	00	00	00	00	00
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N ₂ + Ar	28.013	00	00	00	00	00	00
H ₂ O	18.015	00	00	00	00	00	00
CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
C ₃ H ₈	44.095	00	00	00	00	00	00
C ₄ H ₁₀	58.122	00	00	00	00	00	00
C ₅ H ₁₂	72.150	00	00	00	00	00	00
N ₂ + Ar	28.013	00	00	00	00	00	00
H ₂ O	18.015	00	00	00	00	00	00
CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
C ₃ H ₈	44.095	00	00	00	00	00	00
C ₄ H ₁₀	58.122	00	00	00	00	00	00
C ₅ H ₁₂	72.150	00	00	00	00	00	00
N ₂ + Ar	28.013	00	00	00	00	00	00
H ₂ O	18.015	00	00	00	00	00	00
CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
C ₃ H ₈	44.095	00	00	00	00	00	00
C ₄ H ₁₀	58.122	00	00	00	00	00	00
C ₅ H ₁₂	72.150	00	00	00	00	00	00
N ₂ + Ar	28.013	00	00	00	00	00	00
H ₂ O	18.015	00	00	00	00	00	00
CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
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N ₂ + Ar	28.013	00	00	00	00	00	00
H ₂ O	18.015	00	00	00	00	00	00
CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
C ₃ H ₈	44.095	00	00	00	00	00	00
C ₄ H ₁₀	58.122	00	00	00	00	00	00
C ₅ H ₁₂	72.150	00	00	00	00	00	00
N ₂ + Ar	28.013	00	00	00	00	00	00
H ₂ O	18.015	00	00	00	00	00	00
CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
C ₃ H ₈	44.095	00	00	00	00	00	00
C ₄ H ₁₀	58.122	00	00	00	00	00	00
C ₅ H ₁₂	72.150	00	00	00	00	00	00
N ₂ + Ar	28.013	00	00	00	00	00	00
H ₂ O	18.015	00	00	00	00	00	00
CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
C ₃ H ₈	44.095	00	00	00	00	00	00
C ₄ H ₁₀	58.122	00	00	00	00	00	00
C ₅ H ₁₂	72.150	00	00	00	00	00	00
N ₂ + Ar	28.013	00	00	00	00	00	00
H ₂ O	18.015	00	00	00	00	00	00
CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
C ₃ H ₈	44.095	00	00	00	00	00	00
C ₄ H ₁₀	58.122	00	00	00	00	00	00
C ₅ H ₁₂	72.150	00	00	00	00	00	00
N ₂ + Ar	28.013	00	00	00	00	00	00
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CO ₂	44.010	00	00	00	00	00	00
CH ₄	16.043	00	00	00	00	00	00
C ₂ H ₆	30.070	00	00	00	00	00	00
C ₃ H ₈	44.095	00	00	00	00	00	00
C ₄ H ₁₀	58.122	00	00	00	00	00	00
C ₅ H ₁₂	7						

* Composition of trace components were estimated from reference (1).

compressed in a two stage compressor driven by high pressure fuel gas. After compression, the gas is cooled and the water which condenses is used as make-up in the main cooling towers.

The final stage in the production of pipeline SNG, dehydration, is accomplished by contacting the cool gas with lean glycol in a countercurrent absorber to remove the final traces of water. Rich glycol from the bottom of the dehydrator is distilled to remove the absorbed water. The overhead vapor, consisting of mostly water, is condensed and used as reflux. A side stream is removed to maintain the water balance and is sent to the ash transfer system for reuse. SNG from the dehydrator has a heating value of 980 BTU/scf and is at a pressure of 900 psig, sufficient for pipeline transport.

10.2 POTENTIAL EFFLUENTS

The effluent streams from the methanation section include:

- Pipeline SNG
- Process Condensates
- Waste Heat Boiler Blowdown
- Spent Catalyst
- Fugitive Emissions (equipment malfunctions).

The major pollutants in each of these effluent streams are addressed in section 10.2.1 while the presence of trace constituents is discussed in Section 10.2.2.

10.2.1 Major Pollutants

Pipeline SNG. The synthetic gas feed has had all of the major pollutants removed by the time it reaches the methanation section. All of the potential pollutants which are present in trace amounts will be discussed in section 10.2.2.

Process Condensates. The process condensates are made up of condensates from methanation, compression, and dehydration. Of the three, the condensate from the methanation step is by far the largest, having a flow of 629 gpm. The major pollutants in this stream are CH_4 and CO_2 . The two other streams having flows of about 1 gpm each, have only a small amount of CH_4 . However, the condensate formed in dehydration could have some glycol as well, depending upon the operating conditions within the glycol regenerator.

Boiler Blowdown. The waste heat boiler in the methanation section uses softened water for boiler feed. This inlet stream contains some dissolved solids, consisting mainly of Na^+ , SO_4^{2-} , Cl_3^- and silicates. Only very small amounts of Ca^{++} and Mg^{++} are present. To prevent scaling of the boiler tubes, a portion of the boiler water is removed as blowdown. Since the boiler operates at approximately 100 cycles of concentration, this blowdown stream contains 100 times the inlet concentration of each ionic species. Since no other pollutants are anticipated to be present in the boiler blowdown stream, it is directed to the plant cooling system for use as makeup water.

Spent Catalyst. The pelletized nickel catalyst used in the methanation reaction can be "poisoned" by various contaminants in the gas stream. The expected life, however, is estimated to be from 2 to 5 year (1,2,3). When the efficiency of a reactor is reduced sufficiently, the catalyst will have to be shipped back to the supplier for regeneration. In this state, the catalyst will contain potential pollutants such as sulfur, chlorine and various organic compounds. The replacement of the catalyst could also generate a considerable amount of metallic dust which could be a problem if worker exposure were high. Also, during regeneration, impurities contained in the catalyst may be released to the atmosphere at the supplier's plant. It is difficult to determine the

severity of this problem since the catalyst can absorb a variety of different compounds and because the regeneration only occurs once every 2 to 5 years.

Fugitive Emissions: Fugitive emissions from the methanation section arise from leaks around valves, flanges, connections, etc. No estimate of the quantity of fugitive emissions can be made, although high pressures like those found in this section tend to increase the severity of the fugitive emission problem. Any of the materials present in the process streams found in this section could be released as a fugitive emission.

10.2.2 Trace Constituents

The synthesis gas stream, after washing in a commercial Rectisol unit, contains some hydrocarbons in the C_2 - C_3 range, traces of gaseous nitrogen compounds (NO , NH_3 , HCN , CH_3CN) and sulfur compounds (H_2S , organic sulfur). Some of these trace constituents are absorbed by the catalyst while others end up in the product gas stream. Unsaturated hydrocarbons (ethylene, propylene) are hydrogenated completely on the nickel catalyst and nitrogen oxides are reduced. The conversion of cyanide, however, is incomplete. Table 10-1 shows the estimated distribution of trace compounds within the methanation section.

At temperatures below $300^\circ F$, reduced nickel may react with CO to form nickel carbonyl, which is a highly toxic compound (4). Because of this, the possibility of nickel carbonyl formation at start-up and shutdown is quite high unless certain precautions are taken. Nickel carbonyl has been found in the product gas from the Westfield Lurgi Plant at times other than start up and shutdown (5). Further investigation is required to determine mechanisms of formation and control of this compound.

10.3 CONTROL METHODS

Pipeline SNG. The major effluent from this area is the synthetic natural gas which will be used in a variety of industrial and domestic uses. To reduce the formation of the highly toxic nickel carbonyl, the nickel catalyst should not be allowed to contact CO at temperatures below 300°F. During shut-down, vent gases, should be either recompressed for later use in the process, or sent to the fuel burning section of the plant for use as fuel.

Process Condensates. The largest water stream leaving the methanation section is the condensate from the methanation reaction itself. This stream contains a total of 69 lb/hr CH_4 and CO_2 , and is sent to the water treatment section where air is used to strip off the soluble gases in a packed column. The clean water which results will be reused as soft water within the plant. The condensate from the gas compression step and the water absorbed in dehydration are sent to the main cooling tower and the ash transfer system, respectively, for reuse.

Spent Catalyst. Catalyst dust can be controlled by dumping the catalyst into water and using a bag filter at vent locations. In some catalyst systems, it may be possible to regenerate catalyst without removing it from the reactor. In that case, absorbed impurities will be released to the atmosphere. However, the amount and frequency of these pollutants should be very small.

Fugitive Emissions. To minimize leakage, a tight system must be specified and then maintained properly. Pump and compressor seals are potential sources of leakage and need special attention to keep the leakage to a minimum.

10.4 PROCESS MODIFICATIONS

Sulfur Guard. To safeguard against an upset in the Rectisol system, resulting in excess sulfur going to the methanation catalyst, a sulfur guard system may be required ahead of the methanation system. Typically, a tower filled with zinc oxide is used for such an application. In this process, the H_2S concentration can be reduced to 0.1 ppmv by contacting the gas in a static bed of ZnO to produce ZnS (6).

Charcoal Filter. At Westfield, nickel carbonyl was a problem. A charcoal filter was used to remove it from the pipeline SNG. Depending on the operation, a final filter may be required in the plants to be built in the USA.

REFERENCES

Chapter 10

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2. Product Bulletin of "Catalysts and Chemicals International," Louisville, Kentucky (No date).
3. Telecommunications with Mr. J. Richardson of Catalysts and Chemicals International, October 7, 1976.
4. Technical Bulletin No. C13-036, Catalysts and Chemicals, Inc. Louisville, Kentucky (No date).
5. Ricketts, T. S., "The Operation of the Westfield Lurgi Plant and the High Pressure Grid System," Institute of Gas Engineers J., October, 1963.
6. Nonhebel, G., "Gas Purification Processes," George Newnes Limited, London, 1964.

11. GAS LIQUOR TREATMENT

The gases leaving the main Lurgi gasifier and the fuel gas gasifier are laden with tars, tar oils and naphtha. These gases also contain phenols, H_2S , NH_3 , chlorides, plus a large number of minor contaminants. By-product streams generated from the treatment of these gases are produced at the rate of about 100 tons/hour. Unless these chemicals can be treated or recovered and subsequently utilized, a serious pollution problem can be created.

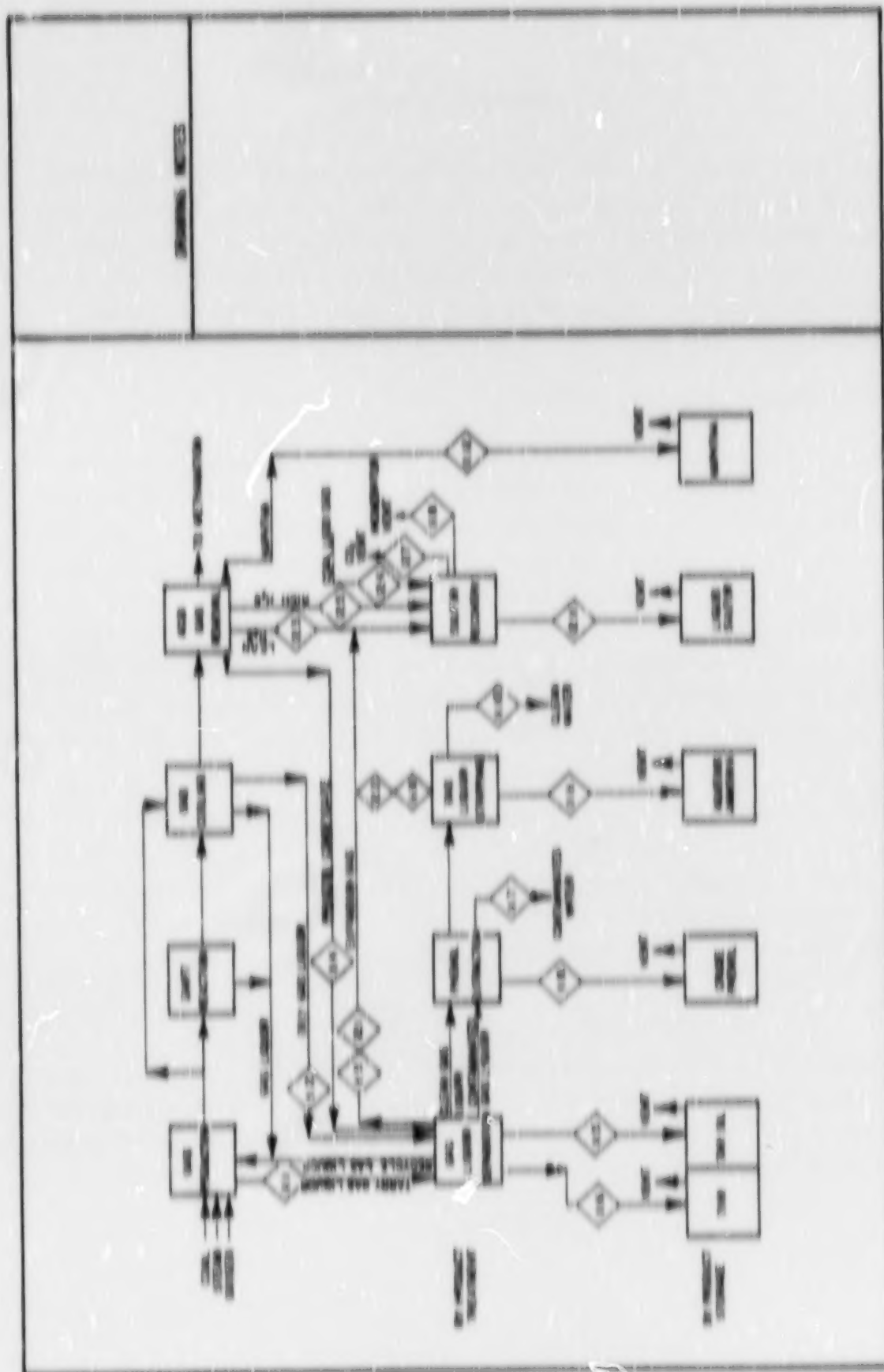
11.1 STREAM FLOWS

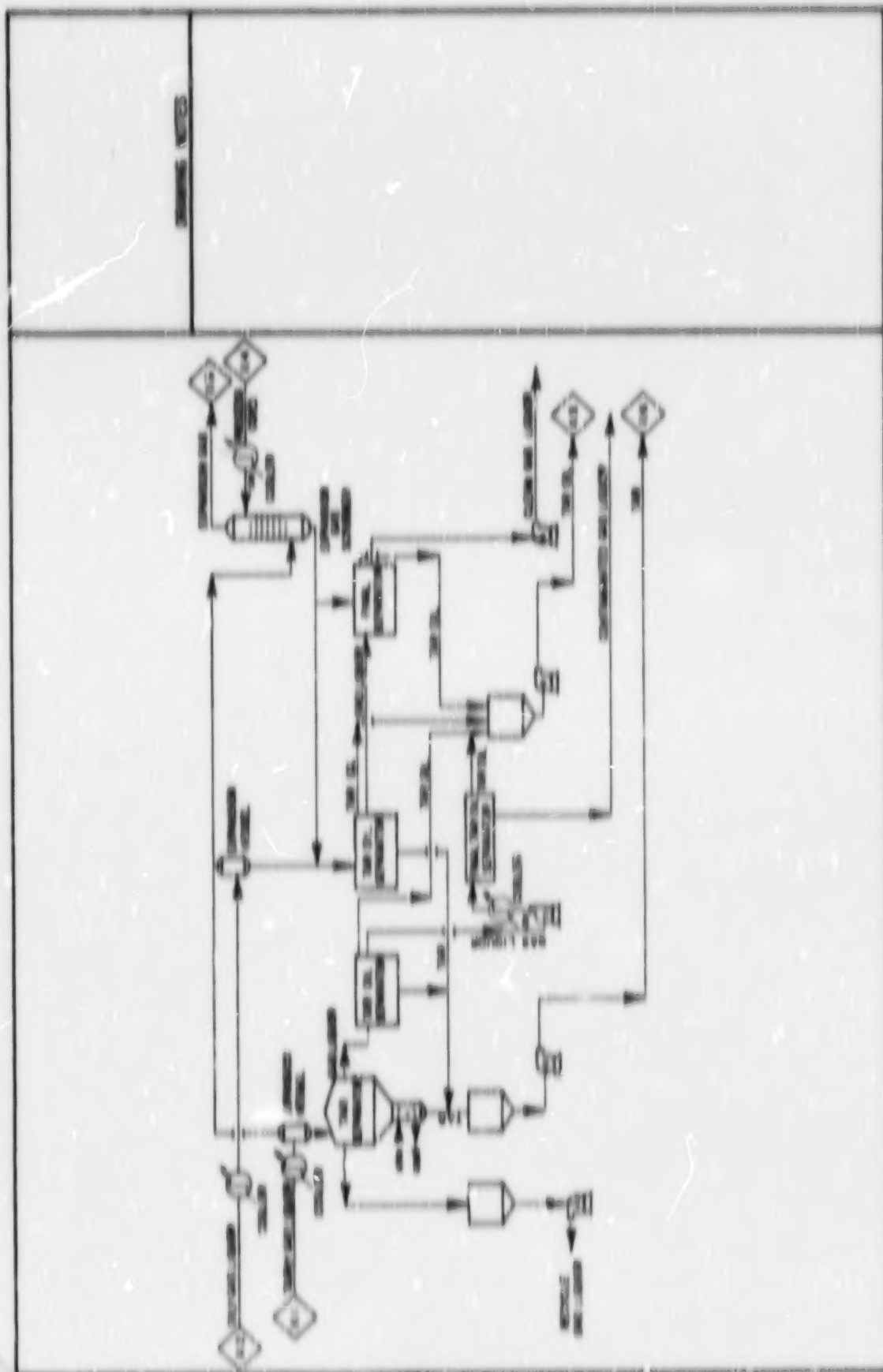
Figure 11-1 shows the distribution of the various by-products throughout the plant. A sizable portion of these by-products are absorbed in or condense out with the organic and aqueous condensates as the gases are first quenched with water and then cooled. The heavier tars separate out first in the gasifier waste heat boiler and are called "Tarry Gas Liquor". Further downstream, in the gas cooling section, the tar oils with the remaining tars condense out forming the "Oily Gas Liquor". In the acid gas removal step (Rectisol Process), H_2S and naphtha separate out. Naphtha is sent directly to the storage tank, whereas H_2S -containing acid gases are processed further to recover the sulfur.

A complete analysis of each by-product area will be presented. Gas liquor separation, phenol extraction, and gas liquor stripping are discussed in the following sections. Sulfur recovery will be analyzed separately in Chapter 12. The process flow schemes for gas liquor separation, phenol extraction and gas liquor stripping are given in Figures 11-2, 11-3, and 11-4 respectively. The material balance for these three areas is presented in Table 11-1.

11.1.1 Gas Liquor Separation

Tarry gas liquor from the gas production section is first depressurized in an expansion tank. The gas evolved from this tank contains mostly CO_2 , water vapor and a small amount of H_2S . This gas is scrubbed to remove any entrained tar products and then sent to the sulfur recovery section for treatment. The

Figure 11-1. *2-Phenyl-1,3-dioxane*



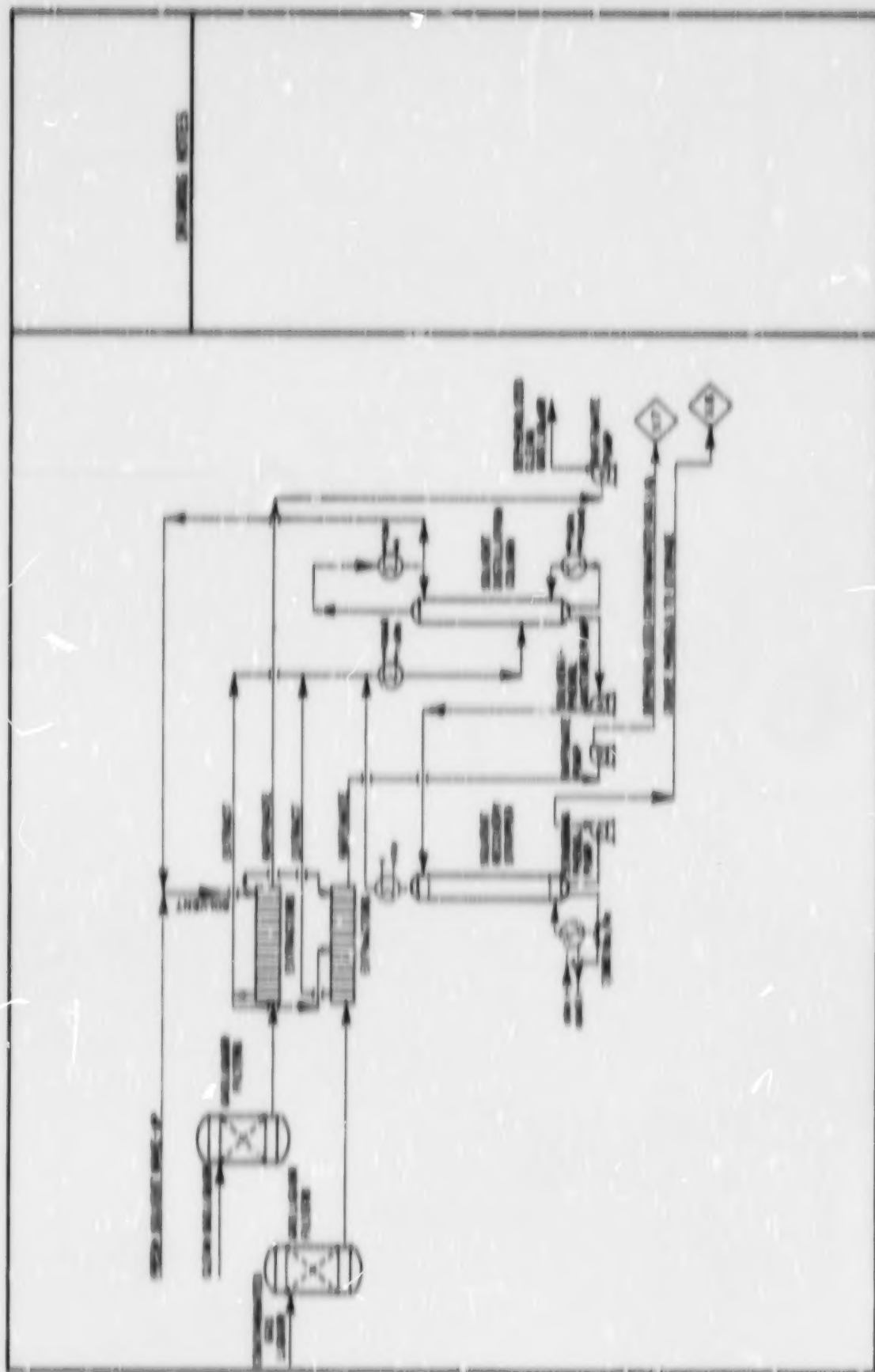


Figure 11-1. GLDA SCHEME FOR PHENOL EXTRACTION - PHENOL/ANISOL PROCESS

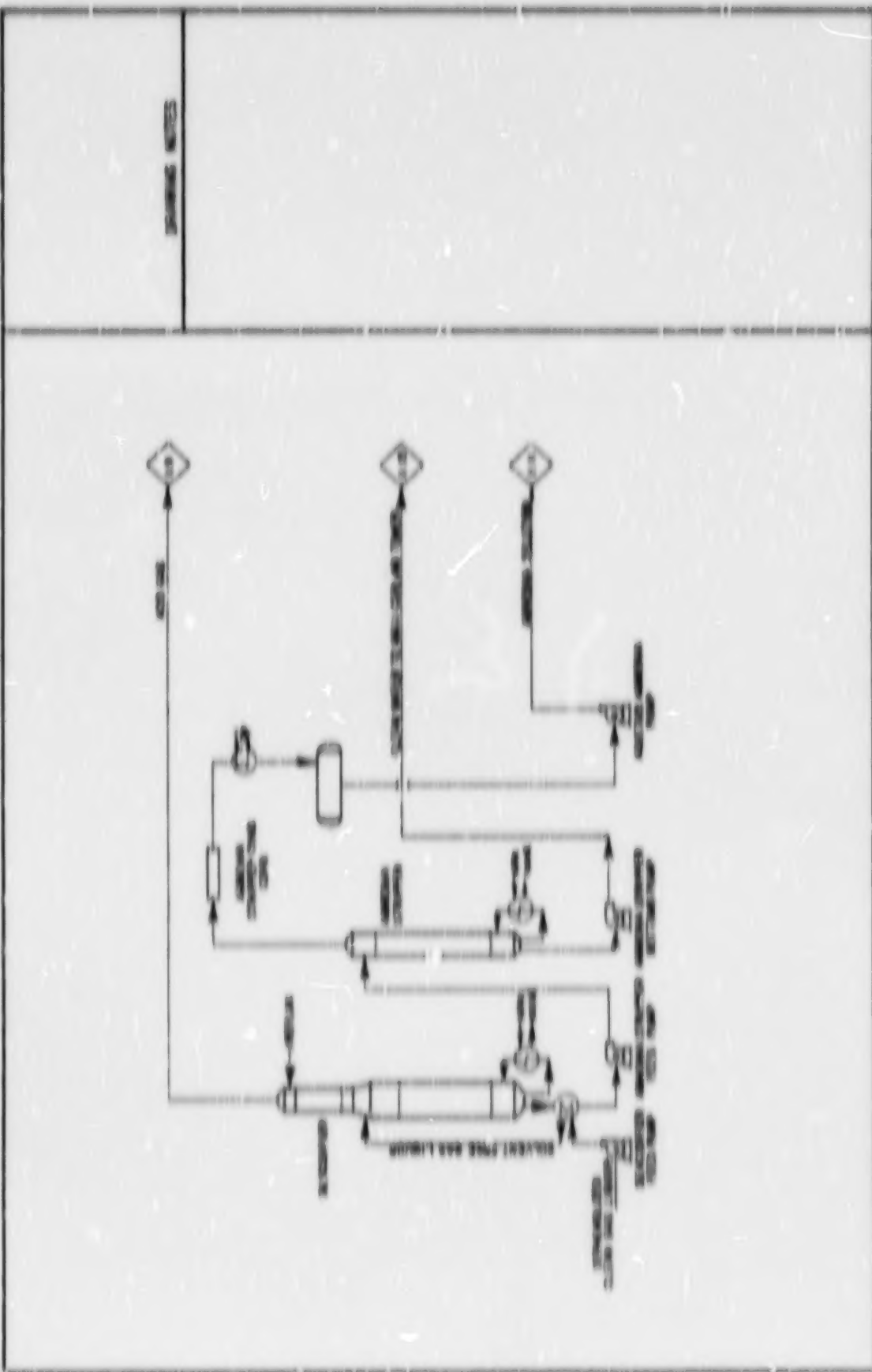


Figure 11-4. FLUID SCHEME FOR GAS LIQUOR STRIPPING

tar and gas liquor from the expansion tank are separated by gravity. The heavy, viscous tars from the bottom of the separator are heated and sent to storage. A portion of the lighter top layer containing tar oil, water and some residual tar is sent to a second gravity separator, and the rest is pumped back to the gasifier for quenching.

In the second separator, residual tar is withdrawn from the bottom, and water and oil are collected separately off the top. The lighter oil layer is withdrawn to storage, whereas the middle aqueous layer termed "Contaminated Gas Liquor" is sent to the phenol extraction area. This stream contains a large amount of organics and dissolved solids which cannot be separated easily.

The oily gas liquor is also flashed separately to remove acid gases. These gases are combined with the vent gases from tar liquor flashing and are treated similarly. Bottoms from the oily gas liquor flash are sent to a tar oil separator. The lighter tar oil layer is withdrawn and sent to the storage tank along with the tar oil from the tarry gas liquor. The heavier aqueous layer, termed "Clean Gas Liquor" is sent to phenol extraction.

11.1.2 Phenol Extraction

Two parallel streams, the clean gas liquor and the contaminated gas liquor are treated to remove various phenols and other organics in a proprietary Lurgi process known as the Phenocolver Process. Both streams are filtered in gravel bed type filters to remove solids, free tar and oil, etc. No information is available on the backwashing frequency of these filters. Filtered liquor is passed through a series of countercurrent extractors using isopropyl ether (IPE) as a solvent. Dephenolized clean gas liquor is sent to the ammonia recovery section. Dephenolized contaminated gas liquor, which is very high in dissolved solids is rejected and sent to the ash dewatering system for reuse.

The extract from both legs of the Phenocolver process are combined and distilled in two stages to separate the IPE from the phenol. IPE from the top of the first distillation column is condensed and recycled to the extractor. Additional IPE is added as required for makeup. The bottoms from the first column are steam stripped in a second column to remove the last traces of IPE from the crude phenol. The overhead vapors from this column are condensed and

recycled to the first distillation column. Crude phenol is pumped from the bottom of the stripper to storage.

11.1.3 Ammonia Recovery

Dephenolized clean gas liquor from phenol extraction still contains phenols, H_2S , CO_2 and ammonia. The first step in the treatment of this liquor is to selectively strip off the acid gases, H_2S and CO_2 . This can be accomplished because the ammonia is tied up with the phenol. The efficiency of this stripping process is greatly dependent upon the solution pH. If the pH is around 9, almost all the ammonia will be tied up as a salt and only acid gases will be stripped off (3). The gases from this stripper are sent to sulfur recovery for treatment.

The dilute ammonia liquor from this step is sent to a second stripping column where the ammonia is stripped with steam at a higher temperature. The overhead vapor, containing 25% ammonia is condensed and pumped to storage. The effluent generated from the bottom of this column still contains small amounts of phenols and organics, and is used as makeup in the main cooling tower.

11.2 POTENTIAL EFFLUENTS

The effluent streams from the gas liquor treatment section include:

- Gas liquor
- Expansion and acid gases
- Tar and tar oil
- Crude phenol
- Dephenolized contaminated gas liquor
- Aqueous ammonia
- Stripped ammonia solution
- Fugitive emissions (equipment malfunctions)

The major pollutants in each of these effluent streams are addressed in section 11.2.1 while the presence of trace constituents is discussed in Section 11.2.2.

11.2.1 Major Pollutants

Gas Liquor. Gas liquors can contain virtually any contaminant encountered within the by-product section. The major contaminants found in the aqueous

layers of the tarry gas liquor and the oily gas liquor at the Westfield Works are shown in Table 11-2.

TABLE 11-2. TYPICAL CONTAMINANTS FOUND IN THE AQUEOUS LAYER AT THE WESTFIELD WORKS(5)

	<u>Tarry Gas Liquor (ppm)</u>	<u>Oily Gas Liquor (ppm)</u>
Sulfide as S	.7	--
Thiosulfate as S_2O_3	9.0	15.8
Cyanide as CN	7.8	2.6
Ferrocyanide as FE (Cn) ₆	4.2	10.5
Chloride as Cl	4.3	11.3
Sulfate as SO_4	90.6	74.1
Suspended Solids	100	340
pH	9.4	8.0

Expansion and Acid Gases. All expansion gases from the tarry gas liquor and oily gas liquor separators and the acid gases from the ammonia recovery section contain H_2S as the major contaminant. These gases also contain H_2O , CO , CH_4 and a large amount of CO_2 . All expansion and acid gases are sent to the sulfur recovery section for treatment.

Tar and Tar Oil. The major contaminants contained in the tar and tar oil at the Westfield Works are described in detail in Table 11-3. Data from the SASOL Plant(5) was also used to estimate the water and coal fines present in tar and tar oil. They were estimated at 3% by weight for both the tar and tar oil. The SASOL information was adjusted for the El Paso coal composition and should be used for order of magnitude purposes only. Sulfur distribution between the tar and tar oil is shown in Table 11-1.

Estimates of the properties of tar and tar oil were given in Tables B-2 and B-3, Chapter B. These tables give the physical properties, distillation range and major components of tar and tar oil as recovered in the Westfield plant. No information is available for the El Paso case, but it should be similar to that given.

TABLE 11-3 ANALYSIS OF PHENOLS IN TAR LIQUOR

ADD OIL LIQUOR
AT WESTFIELD WORKS (3)
February, 1976

	CONCENTRATION, ppm	
	Tar LIQUOR	Oil LIQUOR
Phenols (total)	3,370	5,100
Monohydric Phenols	1,843	4,360
Phenol	1,260	3,100
O-Cresol	155	343
M-Cresol	170	422
P-Cresol	160	302
Total Xylenols	100	393
Monohydric Phenols as Percentage of Total Phenols	52%	85%
Other Phenols		
Catechol	335	190
3-Methyl Catechol	394	80
4-Methyl Catechol	385	110
3 : 5 Dimethyl Catechol	Trace	Trace
3 : 6 Dimethyl Catechol	45	Trace
Resorcinol	272	175
5-Methyl Resorcinol	60	64
4-Methyl Resorcinol	36	--
2 : 4 Dimethyl Resorcinol	Trace	Trace

Tar and tar oil contain a variety of components. These may be used as fuels directly or after refining, reforming or cracking, etc. Similarly, crude naphtha can be used directly as fuel or refined to produce other products such as gasoline. In reprocessing and separating tar, tar oil and phenols into usable components, a certain amount of spillage, leakage and vent losses may occur. Secondary pollution generated from the utilization of these byproducts is discussed in section 2.

Crude Phenol. There is much speculation on the distribution of various phenols, i.e. monohydric (one-OH group) and polyhydric (more than one-OH group) and steam volatile and nonvolatile, not to mention the specific phenols within monohydric and polyhydric classifications. Some data from other plants is available which gives some feel for this distribution. Table 11-3 is the data taken from Westfield Works, Scotland and shows the distribution of phenols in tarry liquor and oily liquor. Tar liquor contains an appreciable quantity of phenols, which is not indicated in the El Paso document. Crude phenol contains many of the same contaminants shown in this table and is sent to storage prior to shipment.

Dephenolized Contaminated Gas Liquor. Table 11-4 gives data from the SASOL plant in South Africa for the combined clean & contaminated gas liquor. Apparently, SASOL does not distinguish between these two since all the liquor is passed through the same extractors. The table gives some idea of the liquor composition before and after the Phenosolvan process. The steam volatile phenols are dramatically reduced from 4,000 ppm to 1 ppm. Unfortunately, information is not given for all the components before and after the Phenosolvan process. Contaminated gas liquor in the El Paso design is very high in dissolved solids concentration and is therefore sent to the ash dewatering system.

Aqueous Ammonia. The aqueous ammonia stream, which is sent to storage, contains 25% NH_3 , some CO_2 and a trace of H_2S . This ammonia is suitable only for fertilizer because it contains CO_2 . For any other purpose, CO_2 will have to be separated.

TABLE 11-4

PHENOSOLVAX PLANT PERFORMANCE
SABOL FACILITY (3)

(For combined clean and contaminated gas liquor stream)

<u>COMPONENT</u>	<u>INPUT</u>
	<u>Concentration, ppm</u>
Phenols	3,250-4,000
Sodium	53
Ammonia (Free)	10,600
Ammonia (Fixed)	150-200
Suspended Tar & Oil	9,000
CN	6
Total S	229
Fatty Acids as $C_{17}H_{35}O_2$	600
CO_2	0.7%

<u>COMPONENT</u>	<u>EFFLUENT</u>
	<u>Concentration, ppm</u>
Phenols (Steam volatile)	1
Phenols (Bound)	60-160
Fatty Acids as $C_{17}H_{35}O_2$	560
Ammonia as Nitrogen	215
Hydrogen Sulfide	12
CN	1
Fluoride	96 mg/l
Chloride	25
Calcium (As Ca)	18
Iron (As Fe)	1 mg/l
Orthophosphate	4.5
Total Dissolved Solids	875
Suspended Solids	21
COD	1,126
pH	8.4

Stripped Ammonia Solution. The clean water discharged from the bottom of the ammonia stripping column contains 20 ppm of monohydric phenols, 760 ppm of polyhydric phenols and 2,700 ppm of other organics. This composition was synthesized based on extraction efficiencies and phenols distribution as suggested by Beychok (1). It is interesting to note however, that SASOL reports that they can reduce the higher phenols down to 20 ppm (8). Therefore, it is possible that the phenols and organic estimates are on the high side. The clean water stream will also contain about 200 ppm of NH_3 , and the other salt and metal contaminants which were discussed in the gas liquor section. The El Paso design proposes to use this water for cooling tower makeup. In view of the organic loading, it appears that the cooling water circuit may become fouled.

Fugitive Emissions. Fugitive emissions from the gas liquor treatment section arise from leaks around valves, flanges, connections, etc. No estimate of the quantity of fugitive emissions can be made, although high pressures tend to increase the severity of the fugitive emission problem. Any of the materials present in the process streams found in this section could be released as a fugitive emission.

11.2.2 Trace Pollutants

The trace components found in coal that appear in relatively substantial quantities in the gas liquor include fluorides, bromides, boron and arsenic. Lesser quantities of heavy metals such as antimony, mercury, lead and cadmium also are present (see Table 5-7 and 5-8). The estimated distribution of trace metals in tar and tar oil based on data from the SASOL plant in South Africa and adjusted for the El Paso design was given in Tables 4-9, 4-10 and 4-11.

11.3 CONTROL METHODS

Gas Liquor. Gas liquor is recycled to the gas production section where it is used as quench liquor. Gas liquor is also recycled to the fuel gas production section where it is used in a similar manner. These processing areas provide adequate control for this stream and are discussed in sections 4 and 5.

Expansion and Acid Gases. The expansion and acid gases generated in this area are further processed in the sulfur recovery section to remove H_2S . The methods for controlling this and other similar streams are discussed in detail in section 12.

By-Products. By-products such as tar, tar oil, crude phenol, aqueous ammonia and naphtha are all pumped to storage, awaiting shipment and/or resale. The effluents generated from the vents of each storage tank and any related control methods are discussed in section 13.

Dephenolized Contaminated Gas Liquor. Contaminated gas liquor from the Phenosolvan Process is very high in dissolved solids. For this reason, it is sent to the ash dewatering system for reuse and eventual disposal. Control methods related to this system are discussed in section 15.

Stripped Ammonia Solution. The clean water discharged from the bottom of the ammonia stripping column is laden with phenols, organics and some ammonia. In view of the organic loading, it appears that the cooling water system may become fouled. Biological treatment of this stream may prove necessary before it can be used as makeup in the cooling system. This possible control method is discussed in detail under Process Modifications, section 11.4.

Fugitive Emissions. Fugitive air emissions are inevitable in any process which contains fittings, valves, flanges, etc. The high pressures encountered in certain areas of the gas liquor treatment section tend to increase the likelihood of having fugitive emissions. While fugitive emissions cannot be completely eliminated, the use of best available technology can help to minimize these emissions. Good maintenance practices also help to minimize fugitive emissions.

11.4 PROCESS MODIFICATIONS

Tar/Oil Separation. The recommended method of separation of tars and oils from the aqueous gas liquors is by flash evaporation followed by API type gravity separators. Under ideal conditions oil can be separated from an aqueous stream to 30 ppm. Other methods of oil and tar separation include (7):

Tar/Water

- a. Filtration
- b. Sedimentation, filtration and flocculation
- c. Centrifuge

Oil/Water

- a. Air Flotation
- b. Gravity separation plus air flotation
- c. Filtration
- d. Centrifuge
- e. Filtration or centrifuge plus heat

Phenol Extraction. The El Paso design specifies the Phenosolvan Process which is liquid extraction using isopropyl ether as the extracting agent. Lurgi claims that the phenol can be reduced to 5-20 ppm in water. Other phenol extraction processes include:

- a. Absorption, counter-current liquid extraction
 - (i) Benzene or light oil process
 - (ii) Tricresyl phosphate process
 - (iii) Holley-Mott process (horizontal flow)
 - (iv) Lowenstein Low Process
- b. Adsorption on solid media
- c. Vapor phase dephenolization
- d. Ion exchange resins

Ammonia Stripping. As mentioned earlier, separation of acid gases from liquor so that ammonia is not lost along with the acid gases, is a pH dependent process. If ammonia can be tied down as a salt with an acid, acid gases can be stripped leaving ammonia salts behind. Phenol is an acid, and if there is insufficient phenol, additional acid such as H_2SO_4 may be required.

Clean Water to Cooling Tower. About 2,300 gpm of water is obtained after recovery of tar oil, phenols and ammonia from the oily gas liquor. This water has substantial amounts of organics and some phenols. It is doubtful that this water can be used in the cooling tower directly. El Paso has simulated

this water composition at the SASOL plant and has been studying the operability of a test cooling tower and heat exchanger for about one year (6). The results of these tests are being used to study the characteristics of the El Paso cooling water system, such as allowable cycles of concentration, foaming tendency, slime build-up in tower, and heat transfer characteristics of the test heat exchanger. Unless these tests prove otherwise, it is felt that biological treatment is necessary before this water can be used in the cooling tower.

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CHAPTER 11

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12. SULFUR RECOVERY

Sulfur is the most important pollutant present in the coal. A large number of processes have been developed over the years to deal with sulfur pollution. Most of these processes were developed for the petroleum industry. In the base case, only Rectisol followed by a Stretford process is considered.

The overall reaction for the Stretford process is as follows:



Figure 12-1 shows the typical distribution of sulfur in the production of SNG and low BTU fuel gas. On a combined basis, 96% of the sulfur present in the coal is recovered as by-product. About 2% of the sulfur is released to the atmosphere, mostly as SO_2 and some as H_2S . The rest of the sulfur appears in by-products such as tar, tar oil, and naphtha (1).

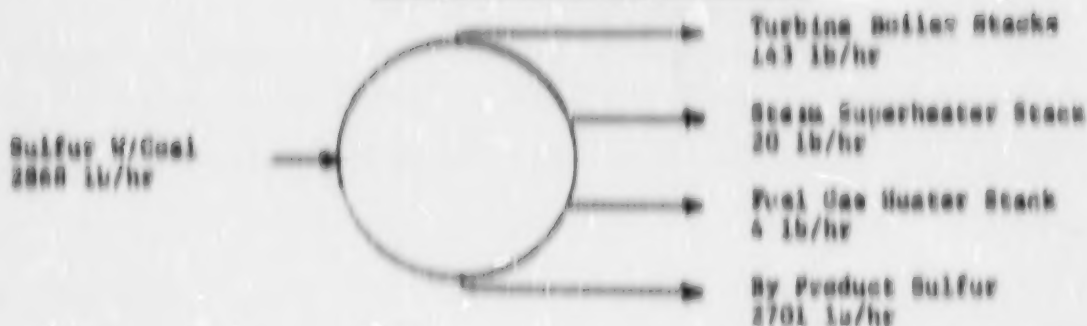
12.1 STREAM FLOWS

Figure 12-2 is a simplified flow diagram showing various streams of the Stretford process. Table 12-1 is the material balance for this process. The rich H_2S stream from the gas purification section along with the coal lock gas from the fuel gasifier are treated with Stretford solution. This solution consists of sodium carbonate, sodium meta vanadate, anthraquinone disulfonic acid (ADA), citric acid and traces of chelated iron at a temperature of 80°F and a pH of 8.5. In the rich H_2S absorber, the H_2S is oxidized by the vanadate to form elemental sulfur. The vanadate, which is reduced by the H_2S , is then reoxidized by the ADA to the pentavalent state. The liquid containing elemental sulfur passes to an oxidizer where ADA is reoxidized by air.

The elemental sulfur/air froth overflows to a holding tank/settler. Reoxidized solution is recycled back to the absorber. Sulfur is recovered from the sulfur froth by filtration, centrifugation, etc. The sulfur is washed with water to remove solution. Finally, water is driven out in the autoclave type melt storage tank where sulfur is stored for shipping. The lean H_2S gas stream along with the expansion gas stream from the tar/tar oil separation, and the acid gas stream from the ammonia recovery section are

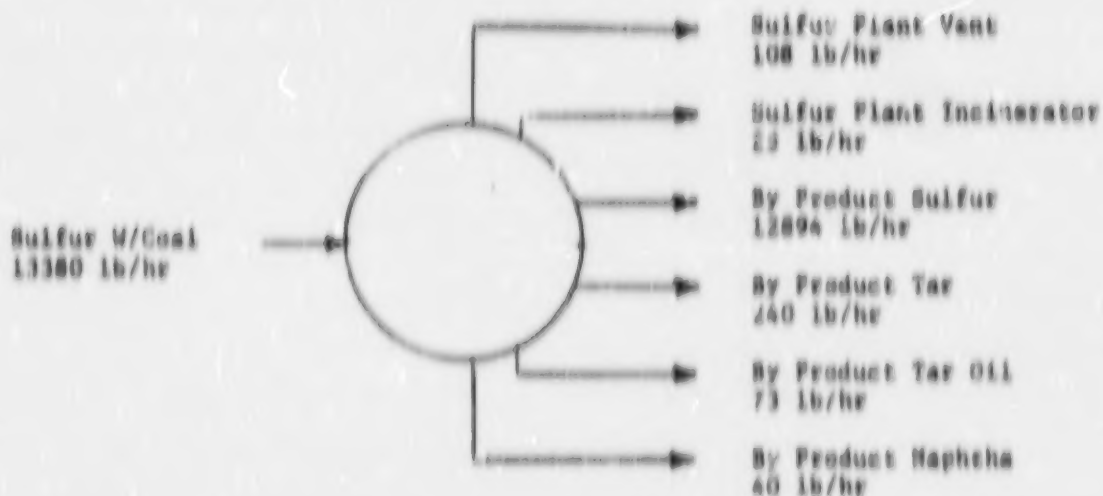
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Sulfur Balance for Manufacture
of Low BTU Fuel Gas



NOTE: Emission Calculates as 0.1306 Lb. SO_2 /MM BTU Fired

Sulfur Balance for Manufacture
of High BTU Gas



- Note: 1) Emission calculates as 0.00792 lb/MM BTU of inlet coal.
2) Sulfur Plant vent is reduced sulfur with concentration less than 100 ppmv.

Figure 12-1. SULFUR DISTRIBUTION

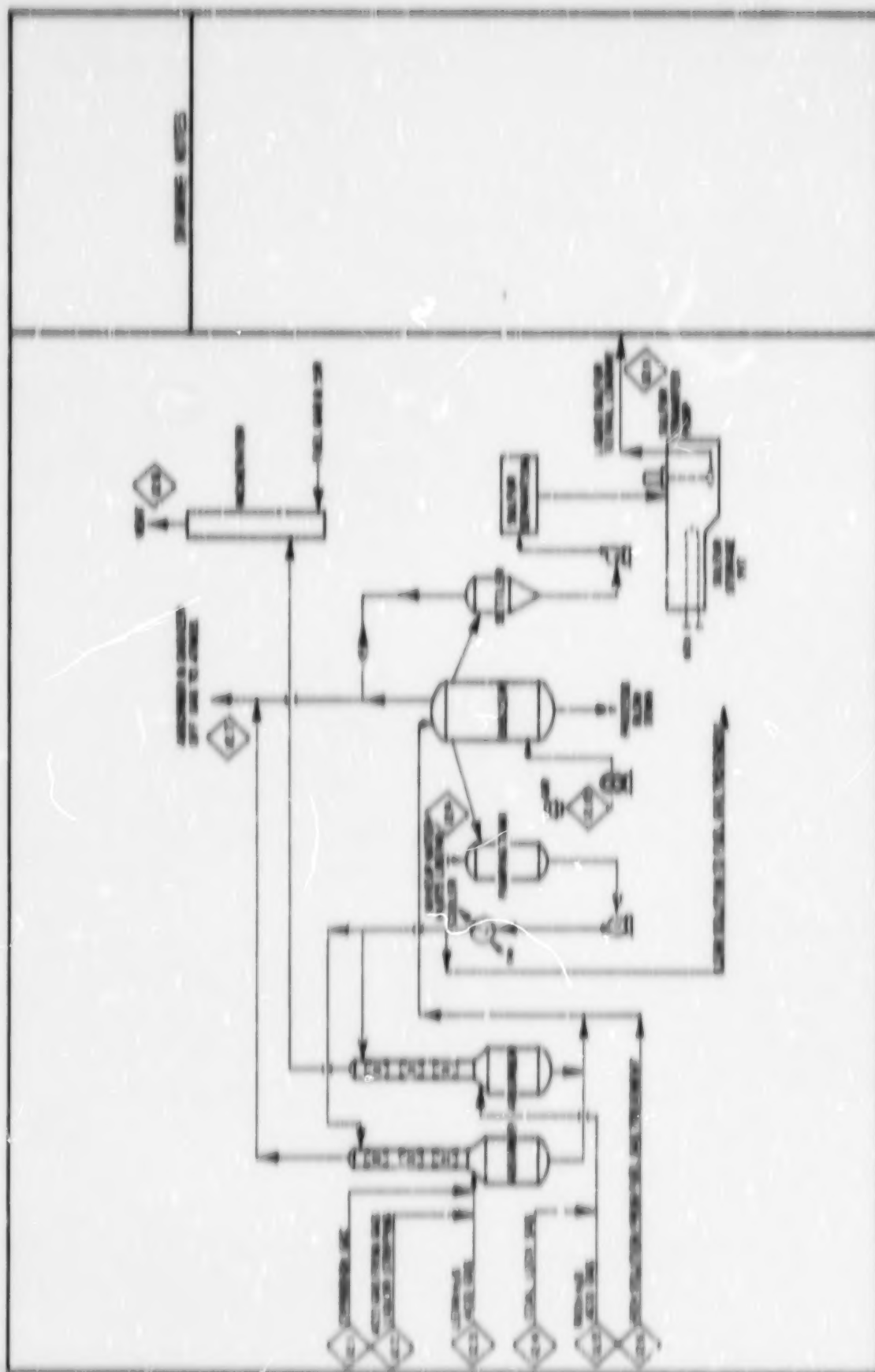


Figure 12-2. FLOW SCHEME FOR SULFUR RECOVERY - SUDREFUR PROCESS

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sent to a parallel absorber called the lean H_2S absorber. Again, the H_2S is converted to elemental sulfur as described above. Vent gases from this absorber are combined with vent gases from the oxidizer and released to the atmosphere. Because of the presence of some hydrocarbons and other pollutants it may be necessary to treat this stream.

Vent gases from the rich H_2S absorber contain considerable H_2S , CO_2 and other hydrocarbons. These gases are incinerated, converting hydrocarbons to CO_2 and water, and the sulfur compounds to SO_2 .

There is no mention of a blowdown stream in the El Paso FPC document. A fraction of the Stretford solution must be disposed of daily due to the formation of the dissolved solids which can accumulate until they interfere with the reaction. These solids are primarily sodium thiocyanate and sodium thiosulfate.

After filtration, the sulfur cake is washed several times on the filter drum to recover soluble reagents. Wash water can be used as a makeup water for the solution. If more wash water is required than can be used for makeup, it is concentrated and returned to the main circulation (2). The El Paso document does not give details of the washing procedure.

12.2 POTENTIAL EFFLUENTS

Referring to Figure 12-2, primary effluents are the streams leaving the Stretford process.

The vent stream (12.7) is a combined stream from the lean H_2S absorber and the oxidizer. Table 12-2 gives the concentration of this stream in ppmv. There is an appreciable quantity of CO_2 (67 ppm) as the Stretford process does not remove CO_2 . Also, there is some H_2S and a trace of CS_2 . The total hydrocarbons concentration is 9,400 ppmv, if CH_4 and C_2H_6 are excluded, the concentration is 2,000 ppmv, which seems quite excessive. Carbon monoxide emissions are 1,600 ppmv. The hydrocarbons, CO and the CO_2 are a source of concern in this stream.

A fraction of the Stretford solution is taken out daily to keep the dissolved solids at a low level. A typical Stretford solution purge contains

TABLE 12-2. GASEOUS POLLUTANTS

Pollutant	Stream (12.7) CO ₂ Vent Gas	Rich H ₂ S ABS. off-gas To Incinerator	Stream (12.8) Incinerator off Gas
	PPMv *	PPMv *	PPMv *
NO _x			76
SO ₂			380
H ₂ S	8.3		
COS	67	610****	
CS ₂	1.9		
Total Sulfur	77	610	380
CO	1,500	72,200	
CH ₄	4,750	21,000	
C ₂ H ₄	2,000	1,070	
C ₂ H ₆	2,650	1,610 ***	
Total Hydrocarbons	9,400	23,700	
Total Hydrocarbons (Excluding CH ₄ & C ₂ H ₆)	2,000	1,070 ***	

* Dry gas only.

** Converted to volume basis as NO₂ from lb./hr in El Paso Material Balance.

*** Does not include methanol losses from rectisol process.

**** Combined H₂S, COS, and CS₂.

sodium salts of anthraquinone disulfonate, metavanadate, citrate, thiosulfate and thiocyanate for which acceptable disposal must be found. The quantity and the frequency of blowdown is not mentioned any place. Nor is there any mention of the disposition and/or recovery of vanadium from that solution.

Rich H_2S absorber off gases are sent to an incinerator to convert hydrocarbons to CO_2 plus water, and sulfur compounds to SO_2 . The final vent stream composition is given in Table 12-1 and Table 12-2. All the hydrocarbons are burned completely. Because of dilution with flue gases, sulfur concentration is reduced from 610 to 360 ppm as SO_2 .

At this time, no information is available about the disposal and/or recovery of the Stretford solution. This can also create a secondary pollution problem. This may become more serious if a larger blowdown is required because of the presence of HCN. When this is the case, there are two methods of operation. In one method, a continuous supply of fresh solution is added so as not to exceed a solids concentration of 25%. In the other method, the concentration is allowed to build to 40% and then the complete charge is dumped.

Table 12-3 shows a breakdown of the major sources of sulfur and hydrocarbon emissions. The total sulfur emissions, excluding boiler flue gases, are 130 lb/hr. This represents 0.6% of the total sulfur contained in the coal fed to the gasifier. It can be seen that the primary source of sulfur released is the carbon dioxide vent stream from the Stretford unit.

Total hydrocarbons, excluding methane and ethane released to the atmosphere amount to 2,390 lbs/hr. The sole source of hydrocarbon emissions is the CO_2 vent stream from the Stretford unit. Hydrocarbons (excluding methane and ethane) released from this stream amount to 6.12 lb per million BTU of coal feed.

12.3 CONTROL METHODS

Vent gases from the Stretford process, particularly from the rich H_2S absorber, contain H_2S , COS and hydrocarbons. The only proven method of hydrocarbon removal is incineration which is very expensive. Another method may be the adsorption of hydrocarbons, so that they can be concentrated and incinerated with less fuel.

TABLE 12-3. GASEOUS SULFUR AND HYDROCARBON EMISSIONS

<u>Stream</u>	<u>CO₂ Vent (12.7)</u>	<u>Incinerator Vent (12.8)</u>	<u>Total</u>
Sulfur			
lb/hr	108.6	25.0	130.6
lbs/lbs in Coal	.0085	.0015	.0080
Total Hydrocarbons			
lb/hr	9,013	0	9,013
lb/MMBTU HHV Coal	.44	0	.44
Hydrocarbon excluding CH ₄ and C ₂ H ₆			
lb/hr	2,390	0	2,390
lb/MMBTU HHV Coal	.12	0	.12

Off-gas from the incinerator may require flue gas desulfurization, depending on SO_2 level. Several processes are available for desulfurization wherein the gases are passed through a venturi scrubber followed by a packed column. Alkaline liquids or slurries such as ammonia or lime are circulated to react with SO_2 , leaving relatively sulfur-free flue gases.

12.4 PROCESS MODIFICATIONS

12.4.1 Introduction

The El Paso design used a Rectisol I unit to produce two gas streams:

- (1) A Lean H_2S stream containing 0.75% ($\text{H}_2\text{S} + \text{COS}$).
- (2) A Rich H_2S stream containing 13.8% ($\text{H}_2\text{S} + \text{COS}$).

Carbon dioxide is the other primary constituent of these streams. The lean H_2S stream contains about 9,000 lbs/hr of H_2S and the rich stream only about 4,000 lb/hr. Both of these streams are treated by the Stretford process.

An alternative to the Stretford process is the Claus process, which can be more economical if the H_2S concentration is greater than 10%. The Claus process has been used extensively in refineries, where the H_2S concentration is typically between 60% and 80%. It cannot be used in conjunction with Rectisol I since only about 30% of the sulfur could be treated.

However, if the Rectisol I unit were replaced by a Rectisol II process, the acid gases would be concentrated by removing about 57% of the total CO_2 . The rich H_2S stream would then contain 10,500 lb/hr of H_2S and the lean H_2S stream 5,500 lb/hr of H_2S . The resulting concentration of the rich H_2S stream would then be 15% H_2S and that of the lean H_2S stream 1.3% H_2S . With this increase in the fraction of total H_2S which appears in the rich H_2S stream, it becomes attractive to treat this stream in a Claus plant. However, the lean H_2S stream still must go to a Stretford plant. Depending on several factors, a Claus plant can remove up to 96% of the incoming H_2S . Therefore, a tail gas treatment is required for the Claus off-gases to achieve higher recovery.

12.4.2 Tail Gas Treatment Classification

A large number of commercial processes are available to treat Claus unit off-gases so that up to 99.9% sulfur recovery is effected. Also, there are

several ways that these processes can be combined to obtain the desired results. There are two basic schemes of combining these treatments as shown in Figures 12-3 and 12-4.

The major differences between Scheme I (Fig. 12-3) and Scheme II (Fig. 12-4) is the location of the incinerator. In Scheme I, all the tail gases from the Claus unit and the Stretford unit are incinerated first and then treated. In Scheme II, the tail gases are treated first and then incinerated. Of course, several variations are possible within Schemes I and II. In either of the schemes, Stretford off-gases can be vented directly to the atmosphere if strict hydrocarbon and CO emission standards are not imposed, since the Stretford process can easily reduce H_2S to less than 10 ppmv. If hydrocarbons and CO concentration limits are set low, incineration of the Stretford off-gases will be required. Also, for some processes of Scheme II, vent gases from the incinerator may require a scrubber to meet the regulations, whereas in others, even an incinerator may not be required. Tail gas treatment may be enough to meet the standards.

12.4.3 Process Selection

As mentioned earlier, a large number of processes are available for tail gas treatment. All of them were developed for the petroleum industry, since the Claus process has been used for over fifty years in this industry. Tables 12-4 and 12-5 give a list of such processes that fall in Scheme I and II respectively. Also given are important characteristics of some of the processes.

One of the main advantages of Scheme I processes is that they can take care of all species of sulfur whether organic, inorganic or sulfur vapors by incinerating them to SO_2 . This means that the tail gas treatment has to remove SO_2 only, as opposed to preincineration treatment where different techniques are used to remove H_2S , COS, CS_2 and sulfur vapors. Also, hydrocarbons are taken care of by burning, and they do not interfere with any treatment process. However, Scheme I has some serious drawbacks. Incineration is an expensive process in terms of fuel cost, though a part of that can be recovered in a waste heat boiler. The volume of gases after incineration increases tre-

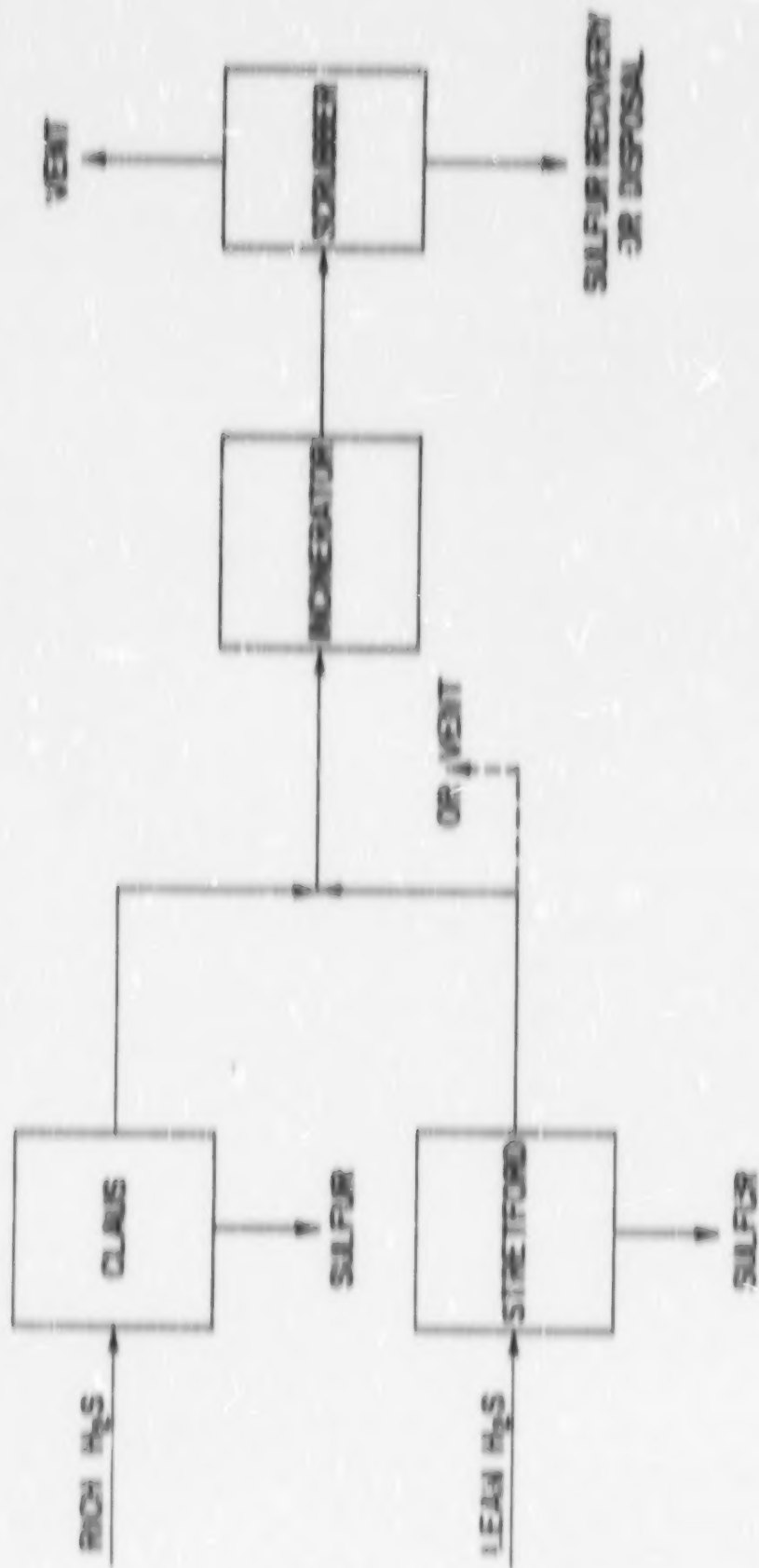


Figure 12-1. SULFUR RECOVERY SCHEME 1 - CLAUSS/STRETTFORD/CONVERTER/VENT

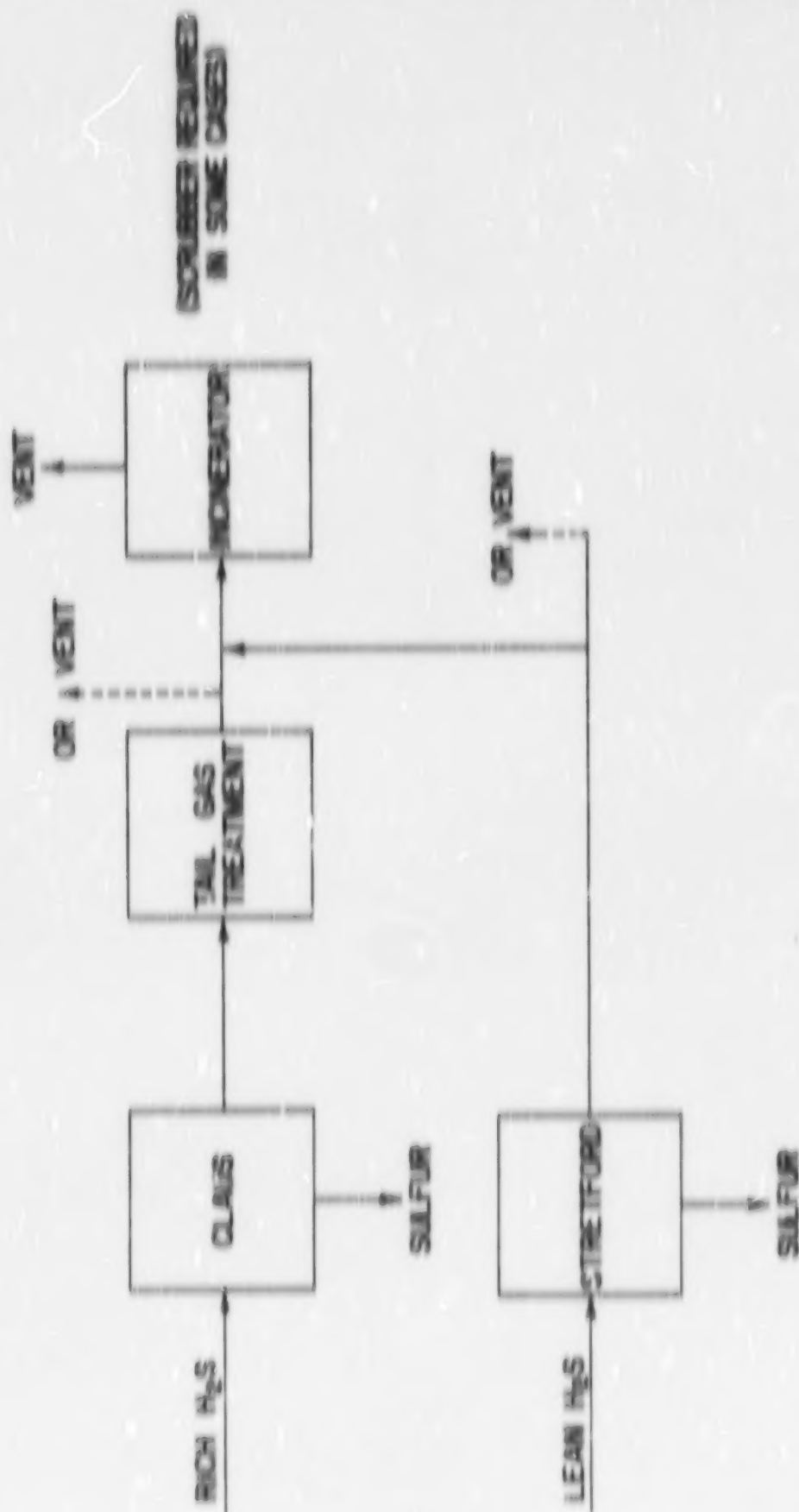


Figure 12-4. Sulfur Recovery Scheme II - Claus/Stretford/Tail Gas Treatment/Condensation

TABLE 12-4. SCHEME 1 - TAIL GAS TREATMENT PROCESSES

<u>Process</u>	<u>Licensor</u>	<u>Application</u>	<u>Description</u>
4-1 SO ₂	Wellman-Lozier Gas, Inc.	Desulfurization of waste gas stream to 100 ppm of SO ₂	All Claus gas burned to SO ₂ . Absorbed in sodium sulfite to form bisulfite. SO ₂ regenerated and sent back to Claus plant or other uses.
IPP I IPP II	Institut Français du Pétrole	Claus tail gas or stack gas clean up to less than 500 ppm	IPP I: Claus tail gas is contacted with a solvent containing catalyst in a packed tower. Sulfur is formed and removed from the bottom. IPP II: Claus tail gas after incineration is scrubbed with aqueous ammonia and clean overhead is incinerated and vented. Sulfur is recovered from the ammonia sulfides and bisulfides.
Oniyoda 700	Oniyoda Chemical Co. Yokohama, Japan	Desulfurization to 500 ppm	Three stages: (a) Incinerated gases are absorbed in dilute sulfuric acid; (b) H ₂ SO ₄ is oxidized to H ₂ SO ₅ with air; (c) acid is reacted with lime stone to form gypsum crystals for use.

Reference: [13]

TABLE 12-5. SCHEME II - TAIL GAS TREATMENT METHODS

<u>Process</u>	<u>Licensor</u>	<u>Application</u>	<u>Description</u>
SCOT	Shell Development Co., Houston, Tex.	Increases Claus recovery to 98.9%; S emission 200-300 ppm	Reduction of all S to H_2S over cobalt/molybdenum, on alumina catalyst at 300° H_2S absorbed in an ammoniacal solution and re-cycled to Claus. Off gas burned.
Basson	Union Oil Co. of California	Clean Claus tail gas	Reduction as in SCOT. All gases taken to a Stretford process.
Clean Air	J. F. Pritchard and Co.	Recovers 99.9% of S from Claus tail gas leaving less than 200 ppm SO_2 equivalent	All forms of sulfur converted to elemental sulfur in three stages. First removes SO_2 , second SO_3 and the third CS_2 .
Sulfreen	SBM/Lurgi; R. M. Parsons Co.	Increases Claus recovery to 99%	An extension of Claus process. H_2S and SO_2 reacted below the dew point in the presence of alumina or activated charcoal. Equilibrium conversion is more favorable as temperature is lowered.

mendously because a large quantity of fuel and air are used to raise the temperature of gases above 1200°F to completely burn hydrocarbons and convert all sulfur to SO_2 . This means that the treatment equipment after the incineration is going to be very large compared to Scheme II processes. Also, the processes for tail gas treatment are more complex in terms of recovery of elemental sulfur. In some cases, a large volume of solid waste containing sulfur has to be disposed of.

In general the Scheme II processes are preferable because of the much smaller gas volume to be handled. In some cases, the final incinerator may not be required because of low H_2S emissions. In those cases, Scheme II processes should be more economical because of incineration fuel savings. The Beavon and SCOT processes are examples of this type of operation. In these processes, all sulfur components of the Claus off-gases are reduced to H_2S . In the Beavon process a Stretford absorber follows the reducing reactor and removes H_2S to 10 ppm. The SCOT process, on the other hand, concentrates the sulfur-bearing components and returns them to the Claus process. The drawback of the Beavon process is that COS and CS_2 are produced in equilibrium concentration and cannot be removed by the Stretford unit. The SCOT process requires incineration of the off-gases because of high H_2S emission (3).

For this study, Scheme II with the Beavon process has been selected for the following reasons:

- (1) The Beavon process requires a Stretford plant as the second part of its processing; however, since a Stretford plant already exists for treatment of the lean H_2S stream, the Beavon process will fit nicely within this setup. Gases from the Beavon unit will add about 15% more load on the Stretford plant. That probably will not change equipment size significantly.
- (2) It will not require an incinerator since a Stretford plant will reduce H_2S to less than 10 ppmv. If strict hydrocarbon emission standards are adopted, an incinerator may be required for the lean acid gas vent.

- (3) It requires only one reactor to reduce sulfur compounds to H_2S .
- (4) There are no waste streams generated, except for a small clean water purge which can be used as part of the Stretford water makeup.
- (5) About 50 lb/hr of hydrogen gas is required for reduction. In its place other reducing gases can be used. A convenient source for the El Paso case is the product gases just before methanation which contain mostly H_2 , CO, and CH_4 .

Fig. 12-5, shows an overall schematic flow diagram of sulfur recovery based on the Claus/Stretford/Beavon process. Table 12-6 is a material balance for the Claus/Stretford/Beavon process. The rich H_2S gas stream from the Rectisol II unit is sent to a by-pass type Claus plant along with a stoichiometric quantity of air to convert 1/3 of the total sulfur to SO_2 . Molten sulfur is the product of the Claus plant. Vent gases from the Claus plant are mixed with a reducing gas to convert all sulfur to H_2S in a Beavon reactor. Gases from this reactor are absorbed in a unit containing Stretford solution.

The lean H_2S gas stream is sent to a Stretford plant, along with the acid gas stream from ammonia recovery and expansion gas from tar/tar oil recovery. To this a small fuel flash gas stream from the treatment of fuel gas with methanol in the Rectisol process is added. Also, added to this stream is the coal lock gas stream from the fuel gasifier. This stream was sent to the rich H_2S absorber in the El Paso design. Since it contains hydrocarbons, it may cause some problems in the Claus plant in terms of carbonization of the catalyst and COS formation. For this reason it has been added to the lean H_2S stream. Elemental sulfur is recovered from the Stretford plant and the off-gases are vented.

12.4.4 Potential Effluents

Referring to Figure 12-5, primary effluent streams are defined as those leaving the Stretford process and Claus plant. The Stretford off-gas stream is vented to the atmosphere unless provision is made for incineration. Table

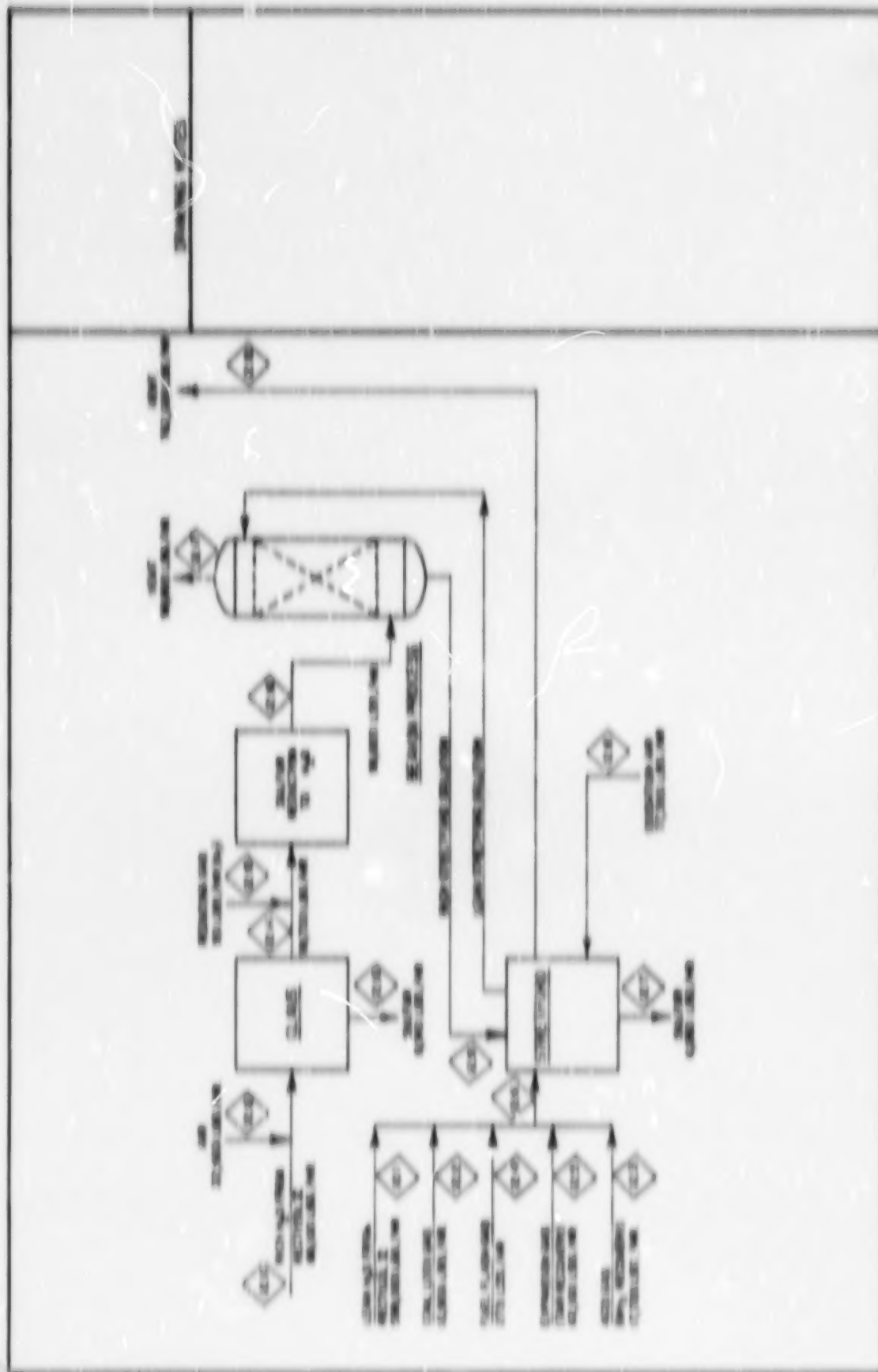


Figure 12-5. FLOW SCHEME FOR SULFUR RECOVERY - CLASS/SULFUR/SULFUR

12-7 gives the composition of the major pollutants in ppmv. It is assumed that the Stratford process can remove H_2S to less than 10 ppmv. COS and CS_2 however, cannot be removed and remain in the off-gas in the concentration of approximately 100 ppmv and 3 ppmv respectively. Hydrocarbons and CO also pass through the Stratford absorber untouched. Total hydrocarbon emissions are quite high (13,200 ppmv or 2,630 ppmv excluding methane and ethane) indicating that this stream might require incineration.

The product and blowdown from the Stratford process were described in section 12.2.1.

The Claus off-gas is sent to a Beavon tail gas treatment process for further sulfur recovery. The off-gas from the Beavon process is considered here as a primary pollutant.

The Beavon process reduces sulfur compounds to H_2S . Most of the development work on the process has been with tail gas from concentrated H_2S type Claus plants. Little data, concerning the concentration of the Beavon tail gas, is available for CO_2 rich tail gas. As was previously mentioned, CO_2 adversely affects the equilibrium between COS and CS_2 , and H_2S . For this type of feed the licensor crudely estimates 150 ppmv COS in the outlet stream (12). H_2S will be reduced to less than 10 ppmv in the Stratford absorber. CS_2 and SO_2 compositions are approximately 20 ppmv each from data based on concentrated Claus off-gas (13). With the above emissions the overall sulfur recovery would be 98.5%.

Table 12-8 shows a breakdown of major sources of sulfur and hydrocarbon emissions for the SN&G and fuel gas production areas. The total sulfur emissions excluding boiler flue gases is estimated to be 86 lbs/hr, or 0.8% of the sulfur in the coal feed to the product and fuel gas gasifiers. This is 1/3 less than the sulfur emissions from the previous case.

Total hydrocarbons, excluding methane and ethane, released to the atmosphere from the sulfur recovery area amounts to 1,350 lbs/hr. However, if the CO_2 vent stream is included, the non-methane and ethane hydrocarbon emissions rise to 3,710 lbs/hr. This is over 50% higher than the previous design case. It appears that hydrocarbons and CO are a major problem and incineration of all vent streams may be required.

TABLE 12-7. COMPONENT CONCENTRATIONS IN VENT STREAMS FROM
CLAUS/STRETTFORD/BEAVON PROCESS
(PPMV)¹

Component	Stretford Vent <u>12.10</u>	Beavon Vent <u>12.17</u>
SO ₂		20 ⁽²⁾
H ₂ S	10	10
COS	100	150 ⁽²⁾
CS ₂	3	20 ⁽²⁾
Total Sulfur	116	220
CO	7,920	
CH ₄	6,670	
C ₂ H ₄	2,630	
C ₂ H ₆	3,940	
Total Hydrocarbons	13,240	
Hydrocarbon excluding CH ₄ & C ₂ H ₆	2,630	

(1) Dry gas only

(2) Concentration of SO₂, COS and CS₂ are order of magnitude only

TABLE 12-4. SULFUR DIOXIDE AND HYDROCARBON EMISSIONS

Pollutant	Steam (12.70) Low Acid Gas Scrub- ber Unit	Steam (12.17) Clas tail Gas Treatment System Unit	Total For Sulfur Recovery	Total Including Reactor Unit
Total Sulfur Sulfur to Atmosphere	69	17	86	86
Lbs. of sulfur to atmosphere per lb. sulfur in coal	0.0042	0.0010	0.0052	0.0052
Total Reactor Hydrocarbons including CH_4 and C_2H_6	5,470	0	5,470	20,450
Lbs. hydrocarbons to atmosphere per million Btu net of coal	0.27	0	0.27	1.0
Total Reactor Hydrocarbons (including CH_4 and C_2H_6)	1,350	0	1,350	3,710
Lbs hydrocarbons (including CH_4 and C_2H_6) to atmosphere per million Btu net of coal	0.066	0	0.066	0.18

* Does not include boiler and heater sulfur emissions.

** Includes sulfur in coal to fuel gas production gasifier.

12.4.6 Control Methods

A simplified scheme of control methods is presented in Figure 12-6. This shows that the lean H_2S gas stream is treated in a Stretford unit. The rich H_2S gas stream is treated in a Claus unit followed by a Beavon unit.

Most of the recovered sulfur, particularly in the petroleum industry, is produced by a modification of the Claus process which was developed about 1890 and involves vapor phase oxidation of hydrogen sulfide with air over bauxite or iron ore catalyst in a single reactor. The first significant advance in the art was made about 1937 by I.G. Farbenindustrie. Instead of burning the H_2S directly over the catalyst, one third was burned completely to sulfur dioxide in a waste heat boiler. In most of the present day plants, H_2S is burned in a non-catalytic furnace to produce sulfur. The furnace is followed by various combinations of condensers, reheaters and Claus catalytic converters to recover additional sulfur.

If the acid gas contains less than about 30% (vol) CO_2 the "straight-through" Claus process is generally chosen (5) (6), and the entire acid gas is sent to the Claus furnace, where H_2S is oxidized under free flame conditions with a stoichiometric amount of air according to the following reactions:



or the overall reaction is



If the CO_2 concentration exceeds about 30%, the free flame combustion with stoichiometric air becomes unstable and the "split-stream" process must be adopted. In this case, the acid gas is divided in the ratio of 2:1. The smaller stream is oxidized completely to SO_2 and then recombined with the larger stream to produce elemental sulfur in catalytic converters. Since in our present case H_2S is only 15%, the rest being mostly CO_2 , split stream operation is the only possibility unless the gases are preconcentrated to about 70% H_2S as is done in the WESCO scheme (10). Figure 12-6 is reproduced from the WESCO scheme. Here, the rich H_2S gas containing 21% (vol) H_2S is concentrated to 70% (vol) H_2S

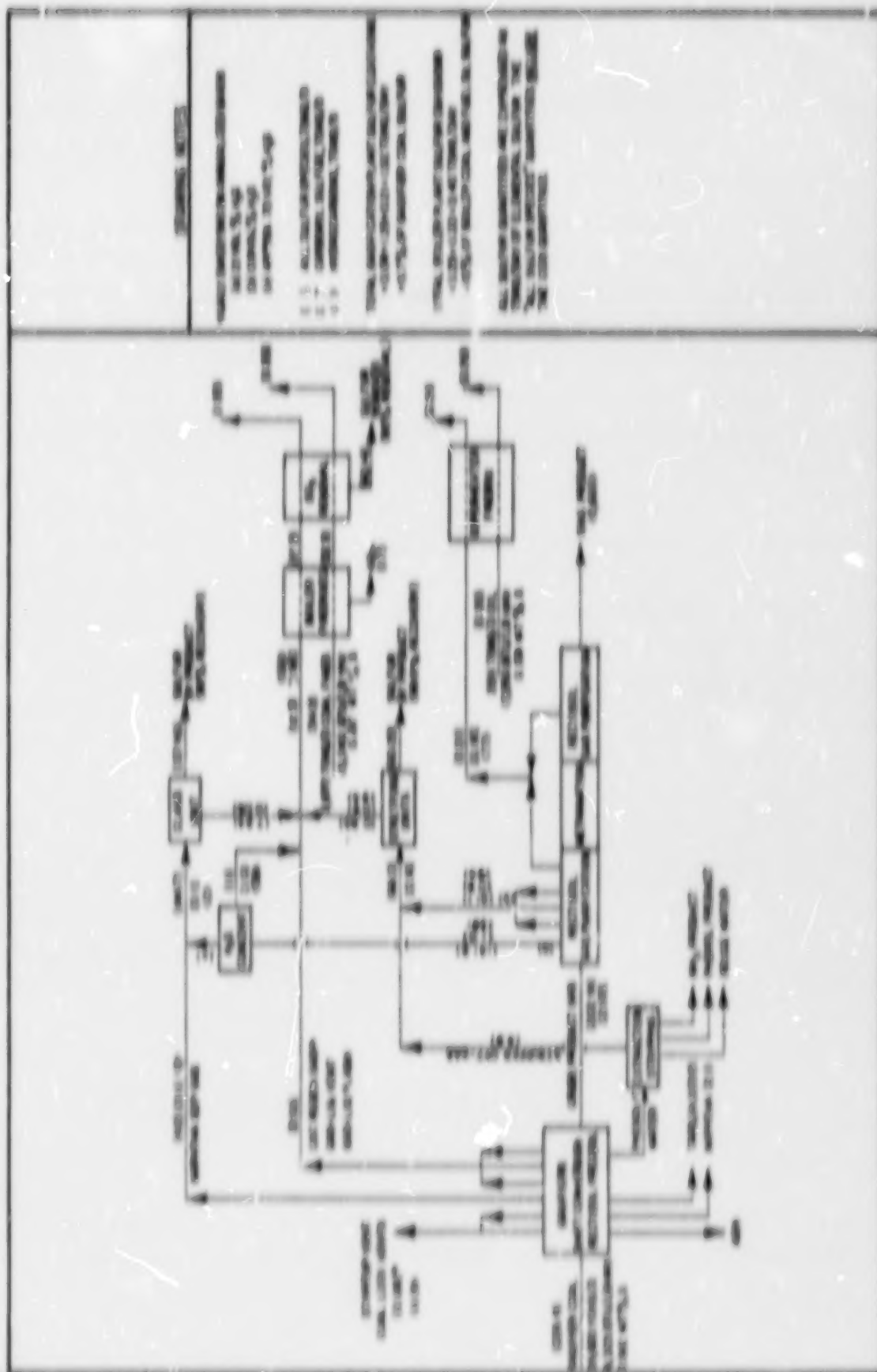
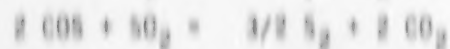


Figure 12-6. SALIC DISTRIBUTION AT DESO. (10)

and then taken to a straight-through Claus unit to recover 95% of the incoming sulfur. The tail gases from the Claus unit are incinerated and scrubbed to remove SO_2 to acceptable limits.

In general, the "once through" flow scheme gives the highest overall recovery if sulfur is condensed before entering the first catalytic converter. This would suggest that the dilute gases should be preconcentrated. However, the preconcentrator may not be justified, if the sulfur recovery in the Claus unit could be increased from 90 to 95% with tail gas treatment. For this reason the "split stream" process is chosen here. Also, with the split stream mode of operation the formation of undesirable by-products such as COS , CS_2 , etc. is minimized.

The types and amounts of hydrocarbons present in the acid gas entering the burner have an effect on the carbon content, and hence the color of the resulting sulfur product. Aromatics and olefins form carbon more readily than paraffins. Also, the amount of carbonyl sulfide formed in the high temperature region is believed to be dependent on the amounts of carbon dioxide and hydrocarbons in the burner feed (6). Some of the reactions that may occur are:



Equilibrium compositions have been calculated for a split stream Claus unit using stoichiometric amounts of air (5). The primary reaction products

are found to be SO_2 and H_2O with virtually no elemental sulfur being formed. The partial pressures of the carbon sulfides are always less than 10^{-6} atm, between 300°C and $1,700^\circ\text{C}$, supporting the contention that they are produced by the reaction between CO and elemental sulfur. This suggests that the coal lock gas stream, which is high in CO and other hydrocarbons, may be added to the split burner directly to convert everything to CO_2 and H_2O . In other words, it is possible that a split stream burner may be used as an incinerator for this small stream.

Figure 12-7 shows a Claus unit with the split stream process. The rich H_2S gas stream is divided in a ratio of 2:1. The smaller stream is burned with air and cooled in a waste heat boiler. Part of this gas stream is used for reheating of gases going to the second and third converter. The rest of it is mixed with the larger stream and sent to the first converter. The efficiency of the Claus plant depends on:

- (1) The number of converters
- (2) The temperature of the converters
- (3) The method of reheating

Obviously, all of these are economic decisions. In general, yield is increased with a larger number of converters and lower reaction temperatures. Temperature is limited by the condensation temperature of the sulfur vapors. Liquid sulfur poisons the activity of the catalyst (7). Also, some plants prefer to run the first converter at a higher temperature than the other converters to increase the conversion of COS to elemental sulfur at the expense of H_2S . The lower temperature of the other converters compensates for this. Also, there are four basic methods of reheat:

- Hot-gas by-pass
- In-line burners
- Gas to gas exchangers
- Indirect heaters, fuel-gas fired

Figure 12-7 shows hot gas bypass for reheating. Vapors from each converter are cooled below the dew point of sulfur to condense out the sulfur and then reheated above the dew point of sulfur by mixing with hot gas from the waste heat boiler. High purity sulfur is obtained as a by-product. The tail gas stream is sent to the Beavon reactor.

A great deal has been written about the Claus catalysts and their activity and poisoning (8), (9). Bauxite has been used as a catalyst for a long time. Deactivation of catalyst due to poisoning may be caused by carbonaceous deposits, sulfur condensation, sulfur vapor adsorption, thermal degradation and sulfate formation. Bauxite contains undesirable iron and silica compounds which are poisoned very easily. An improved version of bauxite is "Porocel" of Engelhard Minerals & Chemical Corp. which is made from high grade activated bauxite. It contains 88 - 92% alumina. Pure activated alumina is being proposed as a better catalyst. In most cases a catalyst life of 2 - 5 years can be expected.

The Beavon process for the treatment of Claus tail gases employs three distinct steps:

- (1) hydrogenation of sulfurous compounds to H_2S in a catalytic reactor.
- (2) cooling of the reactor effluent gases.
- (3) conversion of the H_2S in the tail gas to elemental sulfur by use of the Stretford process.

Figure 12-7 depicts the essentials of this process. The tail gas stream from the Claus plant is heated by exchanging with the reactor outlet gas or by mixing with the hot flue gases and then fed to the catalytic reactor. The catalyst used is cobalt molybdate, which is both rugged and cheap. The reducing gas is hydrogen, or can be supplied by partial combustion of the fuel gas in an in-line burner which simultaneously raises the tail gas stream temperature to the level required for the hydrogenation reactions. The reactor effluent gases are then cooled with water in a direct contact condenser where most of the water vapor is condensed, and at the same time, the tail gas is cooled. The direct contact cooling water is in turn cooled by the cooling tower water in a shell and tube heat exchanger. The purge water produced from

this condenser has good quality and contains only a small amount of dissolved H_2S . With H_2S removal in a small sour water stripper, it is suitable for cooling tower makeup water. This water can also be used as a makeup water for the Stretford solution without any further processing.

The cooled gas then enters the Stretford absorber, where H_2S is removed almost quantitatively.

12.5 OTHER PROCESS MODIFICATIONS

12.5.1 Stretford Solution Blowdown

Because of rapid buildup of solids, a substantial amount of the Stretford solution has to be discarded. There is no mention of this blowdown in the El Paso document. Since no satisfactory disposal methods have been worked out, this could be a serious problem. Also, vanadium is an expensive metal, and will have to be recovered from the blowdown. One of the ways to reduce this blowdown is to put a hydrogen cyanide filter before the Stretford process. This will eliminate the substantial amount of salts which are formed by the reaction of HCN with the Stretford solution.

12.5.2 Hydrocarbon Emissions from Rectisol and Stretford Process

It has been pointed out numerous times that the vent from the Stretford process and the vent from the Rectisol II process are both high in hydrocarbons and CO. If strict hydrocarbon standards are applied it will be necessary to incinerate these streams. Incineration would eliminate the hydrocarbon and CO problem although it would generate some NO_x and convert all sulfur compounds to SO_2 . Incineration, however, is an extremely expensive method of control on such large streams, even when waste heat recovery is included.

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13. BY-PRODUCT STORAGE

13.1 POTENTIAL EFFLUENTS

Approximately 100 tons/hour of various by-products are produced which must be stored and subsequently shipped to buyers. These by-products are tar, tar oil, naphtha, crude phenols, ammonia solution, and sulfur. Following is a breakdown of their production rates:

<u>By-Products</u>	<u>LBS/HR</u>
Tar	68,000
Tar Oil	40,600
Phenols	11,260
Ammonia (as anhydrous)	21,400
Naphtha	20,000
Sulfur	<u>15,582</u>
Total	206,842

Tar, tar oil and naphtha are stored in API type tanks whereas ammonia solution is stored in a pressure vessel. Phenols and sulfur are stored in heated tanks.

Besides these by-products, other chemicals that are used in the process are also stored. These include sodium hydroxide, methanol, iso-propyl ether, sulfuric acid and components of Stretford solution. There may be some other chemicals needed for auxiliary facilities, for example boiler feed water chemicals including amines, chelants, sulfites, etc.

Emissions in this area will consist of tank breathing, leaks, spills and venting of tanks while pumping liquids into the tanks. An estimate of more important emissions based on API design (1) is as follows:

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Crude phenol	1.6 lbs/hr
Tar oil	2.6
Naphtha	2.1
Ammonia	1.6
Product Gases	3.2
Methanol	1.6

13.2 CONTROL METHODS

Process leaks and spills can best be reduced by periodic maintenance checks and adherence to operating instructions. For big spills, concrete dikes with concrete floors around the storage tanks and pump area are required to contain the spills. The vapor emissions from tank vents can be controlled by one or more of the following methods:

Vent Condenser. By circulating refrigerated brine at 0°F, most of the emissions can be reduced substantially.

Scrubbing. Vent vapors can be led to a scrubber where a suitable solvent having low vapor pressure is used for absorbing the vapors. Saturated solvent is either burned or steam stripped to obtain vent vapors in liquid form after condensing the steam and separating the phases.

Incineration of Vapors.

Absorption on Solids such as Charcoal.

REFERENCE

CHAPTER 13

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14. WATER TREATMENT

14.1 RIVER WATER PUMPING PLANT, PIPELINE, AND STORAGE

14.1.1 Stream Flows

Process flow schemes for the river water pumping, pipeline and storage sections are shown in Figures 14-1 and 14-2. A description for each stream within these areas is presented in Tables 14-1 and 14-2. All water required for the complex will be pumped from the San Juan River, 40 miles from the plant site. A bar screen at the intake will collect floating debris. The pumping rate will be sufficient to supply the plant and non-plant water needs of about 3.66 million lb/hr (7,300 gpm). Because the river often carries a high silt load, a settling basin at the pumping station is provided. The settling basin, approximately 400 x 1000 ft will be divided into two ponds. River water can be diverted into either one. Each basin has been sized to provide sufficient retention time and low enough velocity to permit silt and sand to settle from the water. A 40-mile buried, lined, steel pipeline will transfer water from the settling basin to the storage reservoir at the plant site. A trash screen is provided at the pump intake where the desilted water enters the pipeline. Pumps at this station will provide the necessary pressure to transfer the water through the 40 miles of pipeline and overcome approximately 1000 ft. of vertical lift. Raw water from the pipeline will flow into a 210 million gallon reservoir near the plant site. This reservoir, designated raw water storage and pumping, will provide a 21-day storage capacity which is expected to be adequate to maintain plant operations during water pipeline shutdowns caused by emergencies, during periods of low flow in the San Juan River or when the river water is of unusually poor quality. The reservoir will provide for additional settling of silt from the water and will also provide water for fire fighting. This reservoir will be constructed by excavating into a sloping terrain and constructing earthen dikes around the perimeter. The reservoir will be lined to prevent seepage losses. The evaporation rate is expected to average 72,500 lb/hr (145 gpm) from May thru October and 27,500 lb/hr (55 gpm) from November thru April.

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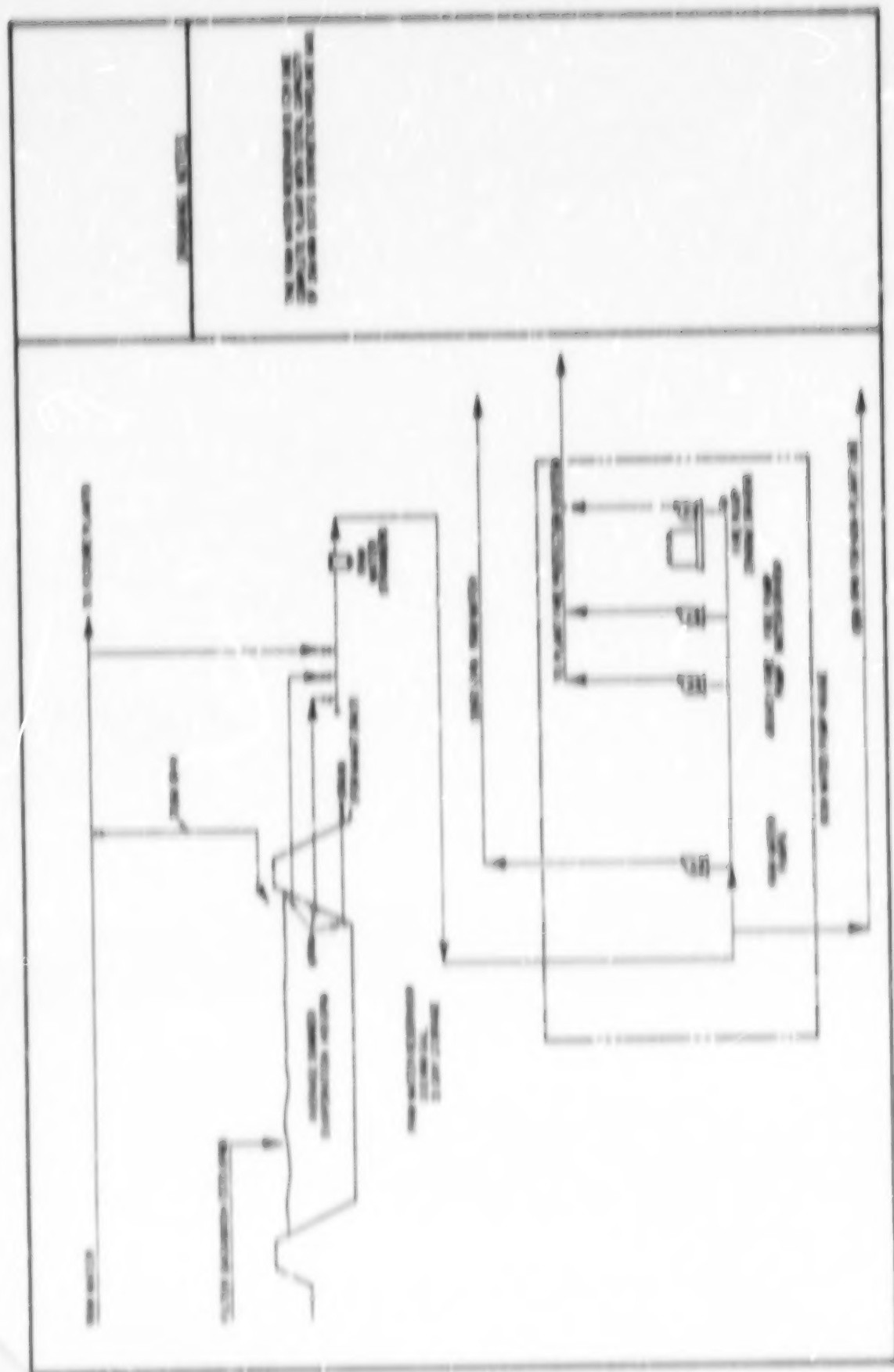


Figure 14-2. 20% AFTER STORAGE AND PUMPING

Table 14-1. RIVER WATER MONITORING POINT AND PIPELINE

Stream	Quantity, lb/yr (avg)	Constituents	Concentration
San Juan River below	1,578,000 (100%)	Calcium, ppm of Ca ion Magnesium, ppm of Mg ion Sodium, ppm of Na ion Bicarbonate, ppm of HCO ₃ ion Carbonate, ppm of CO ₃ ion Sulfate, ppm of SO ₄ ion Chloride, ppm of Cl ion Silica, ppm of SiO ₂ ion Suspended solids, ppm Dissolved solids, ppm Specific conductance at 25°C Carbonate hardness, ppm as CaCO ₃ Noncarbonate hardness, ppm as CaCO ₃ pH	60 9.1 45 140 0 100 14 11 4,300 300 290 121 43 7.9
San Juan River below		Same as above except Suspended solids, ppm	1,500

Table 14-2. RAW WATER STORAGE AND PUMPING

<u>Stream</u>	<u>Quantity, lb/hr</u>	<u>Constituents & Concn.</u>
<u>IN</u>	<u>(gpm)</u>	
Raw water from river water pumping Bldg.	3,528,000 (7066)	See Table 14-1
Filter Back-wash	185,000 (370)	NR
Total, IN	3,713,000 (7426)	
<u>OUT</u>		
To raw water treatment	2,996,000 (5992)	NR
Non-Plant Use	644,500 (1289)	
Evaporation from raw water reservoir	72,500 (145)	
Total, OUT	3,713,000 (7426)	

NR = Not Reported to El Paso Document

In addition to the 3.6 million lb/hr (7,000 gpm) of raw water from the pipeline, the reservoir will also receive 106,000 lb/hr (370 gpm) of filter backwash from the raw water treating area. The raw water pumps will draw water from the reservoir through strainers and deliver 3 million lb/hr (6,000 gpm) to the raw water treating area and 0.66 million lb/hr (1,300 gpm) to non-plant using areas.

14.1.2 Potential Effluents

14.1.2.1 Major Pollutants. It is expected that the only streams with potential effluent problems at the river water pumping station will be (1) trash collected on the screens at the intakes of the pumping station at the river and the settling basin and, (2) silt and sand accumulations in the settling basin.

The pipeline does not appear to have any potential effluent problems. The potential effluents at the raw water storage area will be silt accumulation in the reservoir and waste solids accumulated in the raw water strainers at the intake of the raw water pumps.

14.1.2.2 Trace Constituents. There does not appear to be any potential effluent problem from trace constituents.

14.1.3 Control Methods

14.1.3.1 Proven Methods. Control of (1) trash collected on the intake screens, (2) silt and sand deposited as sediment in the raw water settling basin and in the raw water storage reservoir, and (3) materials collected on surfaces of strainers at pump stations, is not addressed in the El Paso document.

14.1.3.2 Potential Methods. Trash from intake screens could be allowed to dry and then incinerated. Silt and sand deposits from the raw water settling basin and storage reservoir could be used as land-fill. Materials from the pump strainers could also be used as land-fill.

14.1.4 Process Modifications

None suggested.

14.2 RAW WATER TREATMENT

14.2.1 Stream Flows

The process flow scheme and the material balance for the raw water treatment section are given in Figure 14-3 and Table 14-3, respectively.

14.2.1.1 Inlet Streams. This area will receive (1) some 3 million lb/hr (6,000 gpm) of raw desilted water from raw water storage (for analysis see Table 14-1), (2) about 1.5 million lb/hr (3,000 gpm) of hydrocarbon contaminated steam condensate from various sources and (3) about 315,000 lb/hr (630 gpm) of process condensate from the methanation area consisting of mostly water and containing 69 lb/hr of dissolved gases, CO_2 (0.7 moles/hr) and CH_4 (2.4 moles/hr).

The raw water will be treated in a lime softening system (clarifier-treater); alum, polymer and chlorine are also used in this treatment. After treatment the water is stored in a clear well and then pumped through gravity filters filled with anthracite. Filtered water goes either through ion exchange mixed beds or through zeolite softener sets.

The process condensate from the methanation area will be stripped of carbon dioxide and methane by blowing air through it. This stream is then combined with the zeolite softened water.

Other streams entering the raw water treatment area are sulfuric acid and sodium hydroxide for ion exchange regeneration, sodium chloride for zeolite regeneration, zeolite and ion exchange resins for makeup, activated carbon and anthracite.

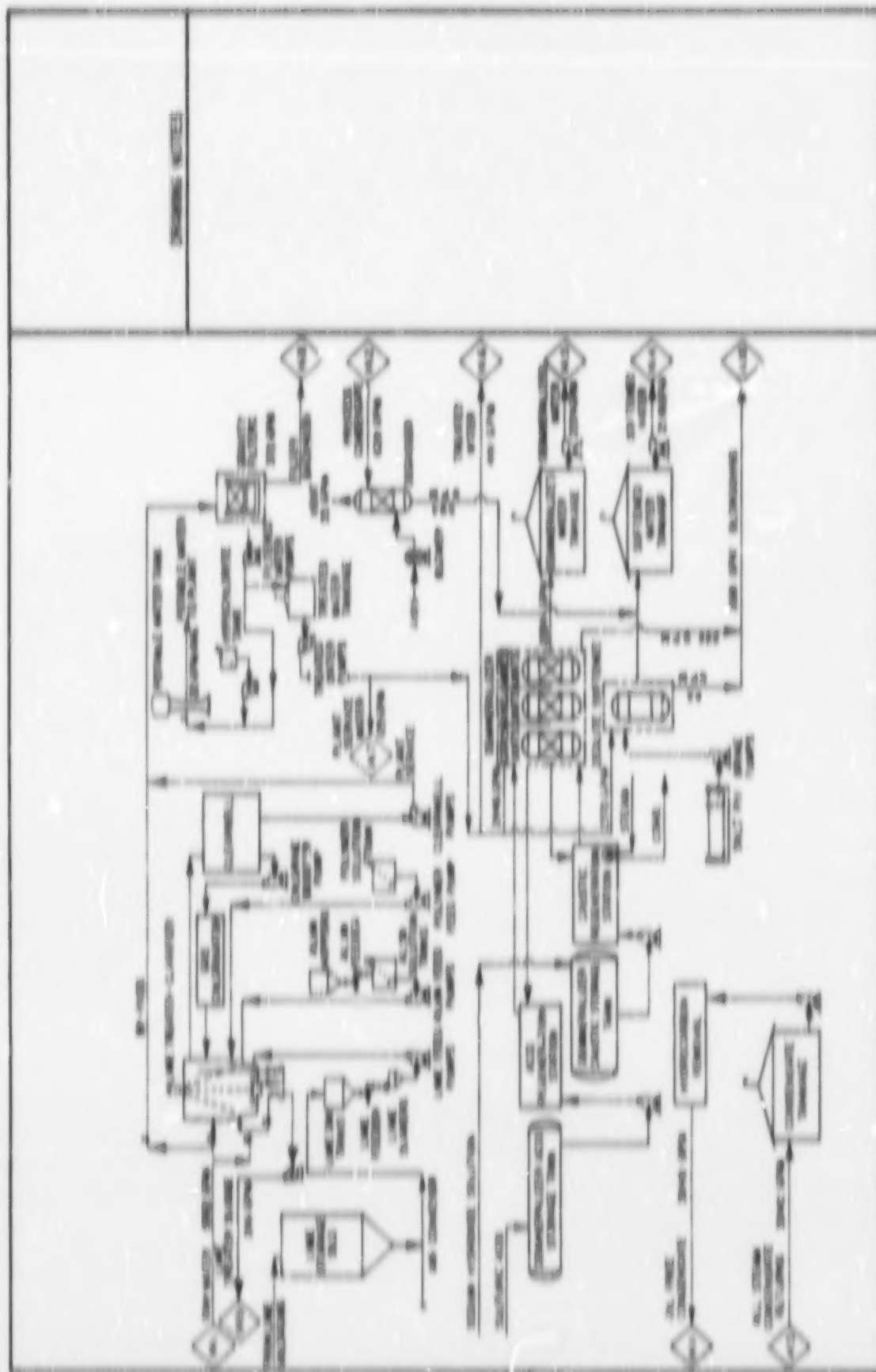


Figure 14-1. Flow Scheme for the Raw Water Treatment Section

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14.2.1.2 Outlet Streams. Water, which has been through the lime treater-clarifier and the gravity filters, is stored in the treated water tanks. Plant service water, potable water, and treated water for makeup in the clean cooling tower are drawn from the treated water tanks. These tanks also supply feed water to the demineralizers and to the zeolite softeners. Demineralized water is sent to steam generators for lower pressure steam generation.

Zeolite softened water is supplied to the methane generation area. The air stripped process condensate stream from methanation is returned to that area. After removal of trace hydrocarbon contaminants the steam condensate stream is returned for use in high pressure steam generation. The lime sludge underflow from the lime treater-clarifier is sent to ash dewatering and transfer. Blowdown wastes from the regeneration of the ion exchange and zeolite units are also sent to the ash dewatering and transfer area. Periodically spent carbon and spent anthracite will be sent to the same area.

14.2.2 Potential Effluents

14.2.2.1 Major Pollutants. Potential pollutants are spent carbon-containing hydrocarbons, lime sludge, blowdown from ion exchange and zeolite regeneration and waste anthracite from the gravity filters. Carbon dioxide and methane are discharged to the atmosphere from the degasser.

14.2.2.2 Trace Constituents. No information is available on trace constituents in the above streams, however the only material that might be suspected of containing hazardous trace constituents is the spent carbon used to absorb hydrocarbons from steam condensate.

14.2.3 Control Methods

14.2.3.1 Proven Methods. No waste streams are discharged to the environment from this area, except the degasser vent which will contain carbon dioxide and methane. All other waste streams are transferred to other areas for disposal. No controls are indicated in the El Paso document.

14.2.3.2 Potential Methods. The carbon dioxide-methane-water vapor vent from the degasser could be collected and the methane reclaimed and returned to the product gas stream.

14.2.4 Process Modifications

The only likely modification for this area is that suggested in 14.2.3.2 above.

14.3 COOLING WATER SYSTEM

14.3.1 Stream Flows

The process flow scheme and the material balance for the cooling water system are given in Figure 14-4 and Table 14-4, respectively. This area serves two functions. The clean cooling towers serve oxygen compression and storage. The main cooling towers serve all other areas in the complex. Circulation rates are 4.1 million lb/hr (8,200 gpm) in the clean towers and 76.4 million lb/hr (153,000 gpm) in the main towers.

14.3.1.1 Inlet Streams. Makeup water to the clean towers will be the boiler blowdown from the process waste heat and power generation boilers. Makeup to the main towers will be (1) "clean" water from gas liquor stripping, (2) treated water from raw water treating, (3) blowdown from the clean cooling towers and treated sewage. Treating chemicals will be fed to both towers to control foaming, corrosion, plant growth, scaling and pH.

14.3.1.2 Outlet Streams. Blowdown from the main towers will be sent to ash dewatering and transfer. There will be entrainment and evaporation from the towers to the atmosphere. A side stream of the circulating water returning to the main towers is filtered. Filter backwash could be discharged with the tower blowdown.

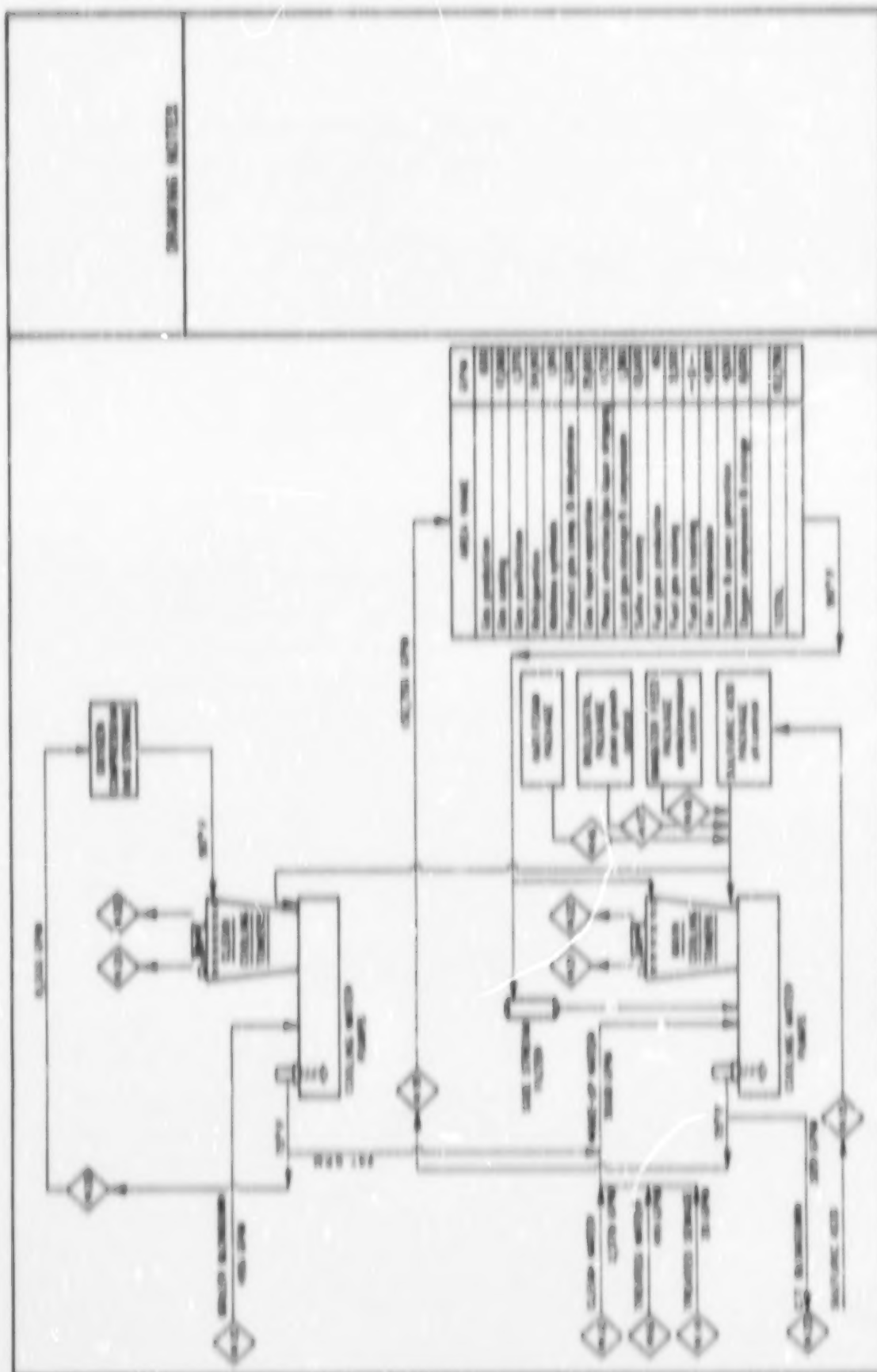


Figure 10.10 The three major types of neurons.

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14.3.2 Potential Effluents

14.3.2.1 Major Pollutants. It should be noted that the blowdown from the cooling towers will contain the treating chemicals, such as chromates, phosphates, algicides, etc. as described in Section 14.3.3.2. Any uncontrolled chemical treatment may constitute a serious source of undesirable pollutants, in addition to those entering with makeup water. The major components and their concentration in the feedwater are listed below. These are expected to be present in the cooling tower blowdown.

<u>Component</u>	<u>Concentration or Range</u>
<u>Present in Feedwater:</u>	
Phenols	760 ppm
Organic Fatty Acids and Oils	2,700 ppm
Ammonia	200 ppm
<u>Resulting from Additives</u>	
Inorganic Chromate Salts	300-600 ppm
Inorganic and Organic Phosphates and Polyphosphates	2-10 ppm
Chromate and Phosphate Combination Treatments	60 ppm
Chlorinated Phenols	300-400 ppm

14.3.2.2 Trace Constituents. There may be trace constituents which are present in the make-up water but are as yet unidentified.

14.3.3 Control Methods

14.3.3.1 Proven Methods. No control schemes are indicated in the El Paso document.

14.3.3.2 Potential Methods. Some components present in the make-up water may be discharged with the blowdown. Treatment chemicals will also be present in the blowdown. Following are some methods which may be used to control these components.

Biological Oxidation Using Water Cooling Towers. Cooling towers have been successfully used as biological oxidation towers and have been particularly effective in oxidizing phenols. In actual operation these systems have achieved 98+% phenol reduction. Operating experience with these systems has been reported as good. Fouling of process coolers by suspended sludge has been prevented by periodic back-washing of the coolers. However, some waste sludge is removed via windage losses. In addition to phenols (750 ppm) the water stream from gas liquor stripping consists of other organic fatty acids and oils, (2.700 ppm) and ammonia (200 ppm).

Inefficient removal of these constituents as waste sludge in cooling towers can result in high losses to atmosphere through evaporation. Hence, the water stream from the Gas Liquor Stripping Area should be biotreated in a separate biological oxidation process before using it as make-up water to main cooling towers.

Control of Treating Chemicals In Cooling Tower Water. The treated water contains salts of sodium (45 ppm), calcium (19.4 ppm), and magnesium (9.1 ppm). The anions will be chlorides (14 ppm) sulfates (168 ppm), silicates (11 ppm), carbonates, bicarbonates and hydrates. When concentrated 3-7 times in a circulating water system, some of the salts will exceed their solubility limits which will result in salt deposition in the form of scale. Sulfuric acid is commonly added in controlled quantities, to the circulating water system to prevent scale formation. The system pH should not be reduced too far below 7.0 to prevent higher corrosion rates.

A variety of treating chemicals, other than sulfuric acid, are used in cooling water systems for corrosion control and for inhibiting the growth of algae and slime. These chemicals do not react with the salts present in the water. Thus, their concentration in the draw-off water will simply be equal to the concentration at which they must be used in the circulating water to perform their function. Following are order-of-magnitude figures for the treating chemicals.

Inorganic Chromate Salts. These are used for corrosion control. Concentration levels may be as high as 300-500 ppm.

Inorganic and Organic Phosphates and Polyphosphates. These are used for corrosion control. Concentration levels are usually at 2-10 ppm. High concentrations of phosphate, under some conditions, can cause the deposition of calcium phosphate scale.

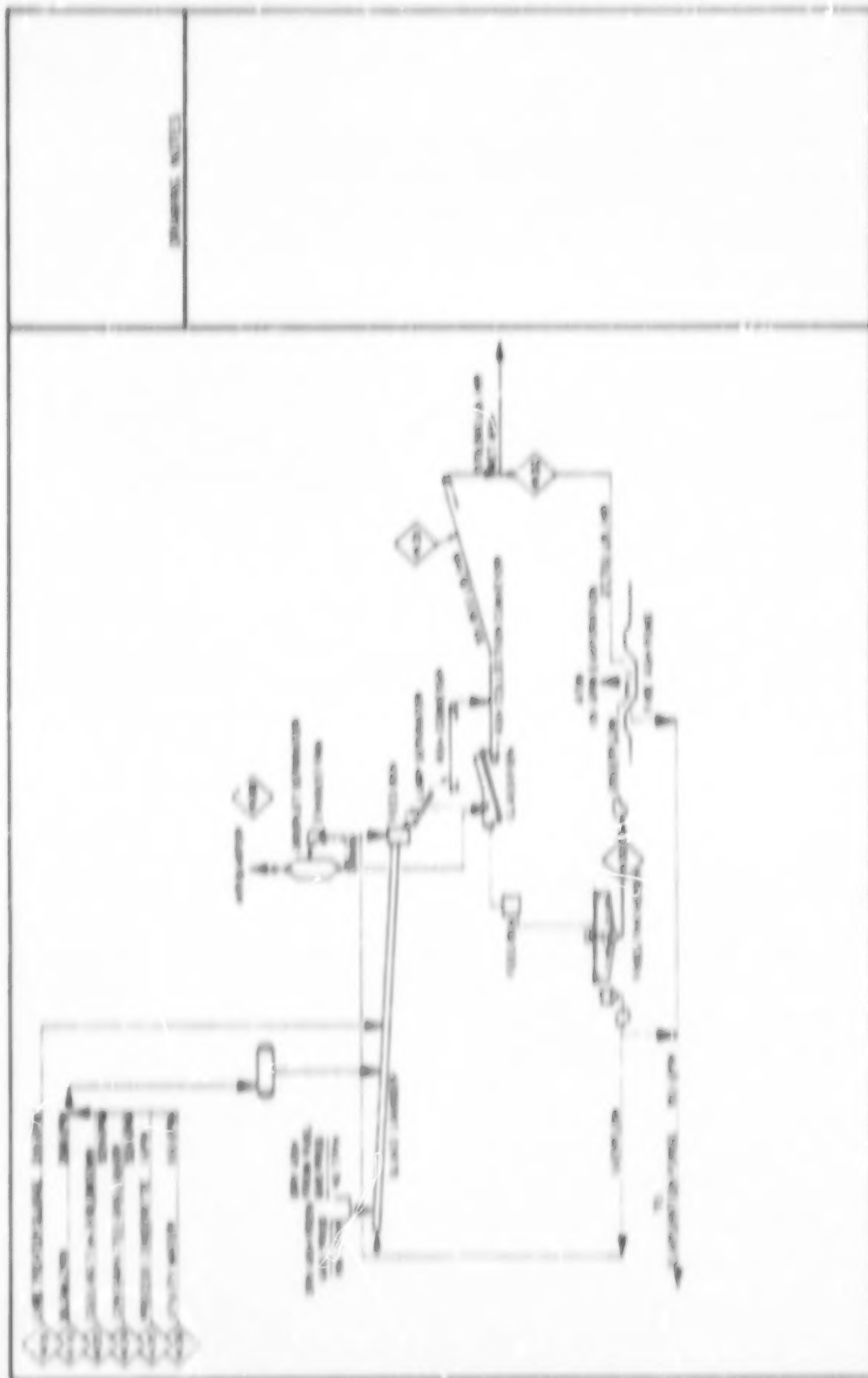
Chromate and Phosphate Combination Treatments. These are used for corrosion control. Total concentration levels may be as much as 60 ppm with CrO_4 ranging from 10-40 ppm and PO_4 from 20-50 ppm.

Chlorinated Phenols. These are used for control of algae and bacterial slime. Intermittent dosage may be as high as 300-400 ppm.

14.4 WASTEWATER TREATMENT

14.4.1 Stream Flows

There is no section in the facility dedicated solely to wastewater treatment. The approach adopted for water disposal is to reuse those streams which require only minimal treatment and to use the more highly contaminated water for ash transport. The ultimate disposal of the ash sluice water then is by evaporation (See Figure 14-5). Some will remain in the wet ash.



DRIVING NOTES

Figure 10-5. PUMP SCHEME FOR THE ASH HEATING AND TRANSFER SECTION

Ash is transported from the high- and low-BTU gasifiers using overflow from a thickener and a combination of blowdown, condensate, and contaminated liquids. Six liquid streams are identified as entering the ash transport system and are listed with stream numbers, origin, and flow rates in Table 14-5.

14.4.1.1 Lime Treater Sludge. Raw water treatment generates a waste stream consisting of lime treater sludge. This stream has a solids content which ranges from 5 to 10 percent, and which includes treatment chemicals (polymer, calcium carbonate, and aluminum hydroxide) and suspended solids present in the raw water (clay, silt and sand). The total stream flow is 216 gpm or 108,200 lb/hr. Components have been estimated for this stream and are listed in Table 14-6.

14.4.1.2 Blowdown. Ion exchange demineralization and zeolite softening are used in the water treatment process. Regeneration of these units results in blowdown which must be disposed of. The blowdown stream flow is 268 gpm, or 134,200 lb/hr. The major constituents in this waste water are sulfate, sodium, chloride, calcium, and magnesium ions. Quantities have been estimated on the basis of the input water quantity and quality and are shown in Table 14-7.

14.4.1.3 Cooling Tower Blowdown. There are two cooling systems designated as "clean" and "main". The clean cooling system services only oxygen compression and storage while the main cooling system services the remainder of the plant. Blowdown from the clean system is combined with makeup water to the main system. Treatment of the water in both cooling systems includes anti-foam agents, biological controls, scale and corrosion inhibitors, and sulfuric acid, pH control. Treatment chemicals used for oxygen cooling towers have to be limited to only those materials which will not initiate any kind of explosion or fire. Residues from each of these will be contained in the main cooling system blowdown which enters the wastewater section. Components which may be present in the blowdown streams as a result of each of the four treatments are shown below.

Treatment

Anti-Foam Agents

Typical Components Used

Aliphatic acids and esters

Alcohols - medium to high molecular weight, mono-and-polyhydric

Sulfonates and sulfates

Nitrogen containing compounds-amines, amides, polyamides

Phosphates - organic phosphates

Silicones

Halogenated Compounds - high molecular weight, highly halogenated

Inorganic compounds

Biological Controls

Chlorine, hypochlorite, chlorophenols

Quaternary amines

Organotin, sulfur, or thiocyanate

Ozone

Scale and Corrosion

pH control inhibitors

Alkaline treatment - sulfonated lignins and tannins, polyacrylates, polyphosphates, polyol esters, and phosphonates

Acid treatment - chromate and phosphate

Chromate, zinc, and phosphate corrosion inhibitors

Silicates and molybdates

Organic polymer - silicate

pH Control

Sulfuric acid

Sodium hydroxide

Table 14-5. STREAMS ENTERING THE ASH TRANSPORT SYSTEM

<u>Stream Identification</u>	<u>Number</u>	<u>Flow Rate</u>		<u>Origin</u>
		<u>gpm</u>	<u>lb/hr</u>	
Lime Treater Sludge	14.9	216	108,200	Raw Water Treating
Blowdown	14.10	268	134,200	Raw Water Treating
Cooling Tower Blowdown	14.23	329	164,700	Cooling Water System
Contaminated Gas Liquor	14.24	329	164,700	Gas Liquor Stripping
Process Condensate	14.25	1	500	Product Gas Compression and Dehydration
Utility Water	14.26	100	50,100	Various Plant Utility Sources

Table 14-6. LIME TREATER SLUDGE COMPONENTS

<u>Component</u>	<u>Rate, lb/hr</u>	<u>Concentration</u>
Polymer	300	0.28%
CaCO ₃	700	0.64%
Al(OH) ₃	320	0.30%
Clay, Silt, and Sand	750	6.93%
Total Solids	8,820	8.15%
Total Stream Flow	108,200	

Table 14-7. BLOWDOWN COMPONENTS

<u>Component</u>	<u>Rate, lb/hr</u>	<u>Concentration</u>
SO ₄	455	3,385 ppm
Na	590	4,402 ppm
Cl	78	579 ppm
Ca	47	349 ppm
Mg	22	163 ppm
Total Stream Flow	134,200	

Table 14-8. CONTAMINATED GAS LIQUOR COMPONENTS⁽¹⁾

<u>Component</u>	<u>Rate, lb/hr</u>	<u>Concentration</u>
COD	185	0.11%
NH ₃	35	210 ppm
Cl	4	24 ppm
H ₂ S	2	12 ppm
CN	0.16	1 ppm
Phenols	70 ⁽²⁾	425 ppm
Fatty Acids	60 ⁽²⁾	360 ppm
TDS	144	870 ppm
SS	4	24 ppm
Ca	3	18 ppm
Fe	0.16	1 ppm
Total Stream Flow	164,700	(pH = 8.4)

(1) Obtained from SASOL data, may be low.

(2) See Table 11-3.

While the above list appears rather formidable, it must be remembered that not all and not even most of the chemical species identified will be present in cooling tower blowdown. As a reasonable estimate, one can assume that an organic anti-foam agent, a biocide (probably chlorine), chromate and phosphate corrosion inhibitors, and sulfate from sulfuric acid pH control may be present.

Cooling tower blowdown contribution to the total ash sluicing wastewater amounts to 329 gpm (164,700 lb/hr).

14.4.1.4 Contaminated Gas Liquor. Contaminated gas liquor, is received at a rate of 329 gpm or 164,700 lb/hr. The major identifiable components of this stream are ammonia, phenols, and fatty acids. COD, TDS, chloride, sulfide, sulfate, and fluoride are also present along with lesser amounts of other materials. A possible stream composition is shown in Table 11-1.

14.4.1.5 Process Condensate. This flow of 1 gpm originates in the final gas compression and drying stage. It contains a trace of glycol drying agent, 0.05 percent. This equals a rate of 0.25 lb/hr of glycol.

14.4.1.6 Utility Water. Utility water originates from various unspecified uses within the plant. These may range from cleanup of equipment and spills to laboratory and sanitary drains. In addition, surface drainage holding ponds will discharge as part of the utility water flow. Prior to being delivered to the ash handling section, utility water is treated in API separators for removal of oil. It is assumed that the major contaminants which will be found in the utility water are small quantities of oil and suspended solids, picked up from surfaces contacted prior to entering the collection system. Most of the oil will be removed by the API separators. The flow to the ash transport system, at 100 gpm or 50,100 lb/hr may contain at intervals as much as 100 ppm of oil. Solids content also will be variable but generally at low levels, under 200 ppm.

14.4.1.7 Wastewater Disposal. Four paths exist for water to exit the ash dewatering area. These are: (1) as water vapor to the atmosphere from the lump separator feed box vent, (2) by evaporation from the main evaporation ponds, (3) by evaporation from the fine ash pond, and (4) as water entrained in the wet ash.

The water stream from the feed box vent results from a water spray introduced into the exhaust from the feed box to contain fugitive dry ash and droplets of slurry. Since the ash is transported wet, the possibility of dry ash entrainment is remote, and scrubbing would primarily remove slurry droplets. A droplet separator or demister is proposed to remove final mist from the exhaust. No significant discharges of either solid particles or liquid droplets are expected in this stream.

The primary exit of wastewater from this plant is by evaporation from the main evaporation pond. This pond is 40 acres in area and receives 901 gpm or 451,000 lb/hr of water from the thickener overflow. To maintain equilibrium, evaporation must occur at a rate of 0.005 gallons per minute per square foot. This water will contain some portion of all constituents of the entering component streams, as well as components leached from the ash during use as transport water. Components of the ash transport water are listed in Table 14-9.

Two phenomena may occur during ash transport by the water. These are the leaching of components of the ash into the transport water and the removal of constituents present in the water by the ash. Depending upon the rates of these processes the resulting thickener overflow stream may be of higher or lower quality than stream 14.27.

An indication of the potential for leaching constituents from the ash may be obtained from Table 14-10. This data was obtained from coal burning power plants, using hydraulic ash transport systems.⁽¹⁾

Table 14-9. INLET ASH TRANSPORT WATER, NET COMPOSITION

<u>Components</u>	<u>Rate</u>	
	<u>lb/hr</u>	<u>Percent</u>
Total Solids (dissolved and suspended)	9,000	1.4
SO ₄ , Cl, H ₂ S, CN	540	0.9
Na, Ca, Mg, Fe	662	0.10
NH ₃	35	56 ppm
Organics (oils, fatty acids, phenols, and glycol)	135	0.02
Total Stream Flow	622,400	

Table 14-10. COMPONENTS OF ASH TRANSPORT WATER

<u>Constituent</u>	<u>Ash Transport BLOWDOWN EXAMPLE 1</u>	<u>Ash Transport BLOWDOWN EXAMPLE 2</u>	<u>Settled Ash Transport Water</u>
BOD ₅	3.0	1.2	1.0
COD	1235.0	290.0	43.1
Chromium	0.37	0.12	0.02
Chromium + 6	0.030	0.009	0.011
Copper	0.16	0.20	0.2
Cyanide (Total)	0.005	0.112	0.012
Iron	76.0	6.2	0.33
Nickel	0.24	0.03	0.03
Oil and Grease	1.0	1.0	1.0
Phosphate (Total)	3.4	0.02	0.02
Zinc	0.55	0.08	0.02
Total Solids	1532.0	3545.0	3050.0
Dissolved Solids	388.0	1894.0	2980.0
Suspended Solids	1144.0	1651.0	70.0

(1) Source: Development Document for Pretreatment Standards
The Steam Electric Power Generating Industry, Hittman
Associates, Inc., Unpublished.

14.4.2 Potential Effluents

The El Paso design has no aqueous effluent return to the San Juan River. All water which is not reused is disposed of by evaporation. The two ponds used for this handle a total of 1,052 gpm or 526,700 lb/hr. Thickener underflow carrying approximately 25% solids is settled in the fine pond from which 151 gpm or 75,600 lb/hr of water is estimated to evaporate (periodic solids removal will be needed). The main effluent from the thickener, the overflow, goes to the main evaporation pond. Evaporation at a rate of 901 gpm or 475,100 lb/hr will be required to maintain equilibrium.

14.4.2.1 Major Pollutants. In the proposed system the major pollutants capable of producing damage are dissolved solids and organics (phenols, oils, tars, and solvents).

It has been claimed that use of wastewater to transport ash results in lowered organic contents. This is indicated by SASOL. Adsorption of organic components may in fact occur but this requires substantiation. If this is an effective treatment the organic residues may then become a potential solid waste disposal problem.

An opposite effect, leaching components from the ash is a probable source of additional dissolved solids loading in the streams to the evaporation ponds. Because the mineral matter discharged from Lurgi gasifiers has not been subjected to temperatures above the ash fusion point and because in addition it has been exposed while hot to an oxidizing atmosphere, it is possible that reactive metal oxides may be present. Upon contact with water these could form soluble hydroxides and potentially cause additional leaching of other metals.

The major components of particular concern are the alkali metals. These, if leached, may raise the pH, and further leach other trace elements from the ash. The entire question of ash leachability requires definitive study.

14.4.2.2 Trace Constituents. As with major pollutants, the trace constituents of concern will be dissolved solids and organics.

Trace elements leached from the ash or having originated from contaminated streams to the ash sluiceway will include any or all of those present in the coal.

Traces of ammonia and sulfide will be present in the water. Cyanide may be present in trace amounts as well.

Trace organic components other than the major organics will include 0.25 lb/hr of glycol. Depending on the degree of adsorption of organics by the ash the total organic contribution may be reduced to a trace level.

14.4.3 Control Methods

14.4.3.1 Proven Methods. The control of wastewater effluents provided for this plant consists of a no discharge design. Evaporation is the only means for water to be removed from the system. If total containment of the contaminated water is achieved, this can be considered a proven method.

A secondary exit of water from the plant is by evaporation from the fine ash pond. This receives underflow from the thickener. Solid content has been estimated at 25 percent. The rate of evaporation is shown as 151 gpm. Based on a 13 acre area, the evaporation rate is 0.0003 gallons per minute per square foot or 0.13 pounds per hour per square foot. The same considerations apply to the water entering this pond 75,600 lb/hr, however, 25,200 lb/hr of solids are carried with that water. Periodically these solids will require removal and ultimate disposition. Assuming that the net solids contain 10 percent moisture when removed from the fine ash pond, an average rate of 27,700 lb/hr of material (consisting of 25,200 lb of solid ash and 2,520 lb of water) must be disposed of to the wet ash conveyor.

The wet ash conveyor then receives from the ash collection system 450,800 lb/hr of ash with 93,500 lb/hr water, and 7,500 lb/hr (dry) lime sludge and from the fine ash pond 25,200 lb/hr of ash with 2,520 lb/hr water. Thus, a total of 96,000 lb/hr water contained in 483,500 lb/hr of solids (476,000 lb/hr of

ash and 7,500 lb/hr of lime sludge) is delivered by the ash conveyor to the ash handling area.

Total containment requires no release of wastewater; however, two potential escape routes from the impoundments exist. One such route is by accidental breaching of the pond barriers either through overflow or by physical damage to the dikes. Such releases would be readily observed and could be limited in extent by appropriate emergency measures.

Of more potential danger is the possibility of permeation of contaminated water through the evaporation pond bottom. Leaks through the bottom would expose groundwater in the area to all dissolved components in the pond and under extreme conditions could potentially transport solids as well.

Proper construction of the ponds will alleviate these two possible sources of unintentional pollutant releases. Sizing the ponds to permit evaporation at the required rate will be necessary. Incorporation of an impervious liner in the main evaporation pond will be necessary to assure leak proof conditions for the pond life. In addition, the fine ash pond must be constructed to permit periodic solids removal. Finally, at the termination of the operation, permanent stabilization of the residues -- precipitated and settled solids -- will be needed. Site geography and climate will have an overpowering effect on design criteria.

14.4.3.2 Potential Methods. Water entering the evaporation ponds is expected to have a possibly high COD. Pretreatment to reduce the organics loading may be an effective method of preventing subsequent development of offensive odors. As previously indicated, the unresolved effectiveness of ash as a absorbent for organic constituents may reduce this potential problem.

14.4.4 Process Modifications

Potential process modifications are treatment of the streams entering the ash handling system to remove organics, or the introduction of a full treatment system with reuse of its effluent. The cost, benefits, and effectiveness of such modifications need to be evaluated.

15. SOLID WASTES

15.1 STREAM FLOWS

15.1.1 Ash Dewatering Transfer

Figure 15-1 is a schematic flow diagram of ash dewatering and transfer facilities. These facilities will be designed to handle all of the ash discharged from the air blown and the oxygen blown gasifiers. Ash will be discharged dry and hot from the individual gasifier ash locks into a sluiceway. Water flowing in the sluice launder will quench and transfer the ash to classification and dewatering equipment. The coarse dewatered ash will be transferred on a belt conveyor to the mine ash handling area for disposal in the mine.

Fine ash from the classification step and the main water stream will be sent to a thickener. The underflow containing the ash fines will be sent to a fine ash pond. The El Paso document does not indicate what disposition is to be made of the fine ash in the pond nor at what frequency but accumulation may be some 12.5 tons/hr. It may be necessary to remove fine ash on a fairly regular if not continuous basis from the fine ash pond and send it to the mine along with the wet ash stream.

Major component and trace element flow rates for the dry ash to this area were given in Tables 4-5 and 4-8, Chapter 4, and Tables 5-4 and 5-6, Chapter 5. Total flows are given in Table 15-1.

15.1.2 Mine Ash Handling

Figure 15-2 shows the mine ash handling area and Table 15-1 defines the inlet and outlet streams.

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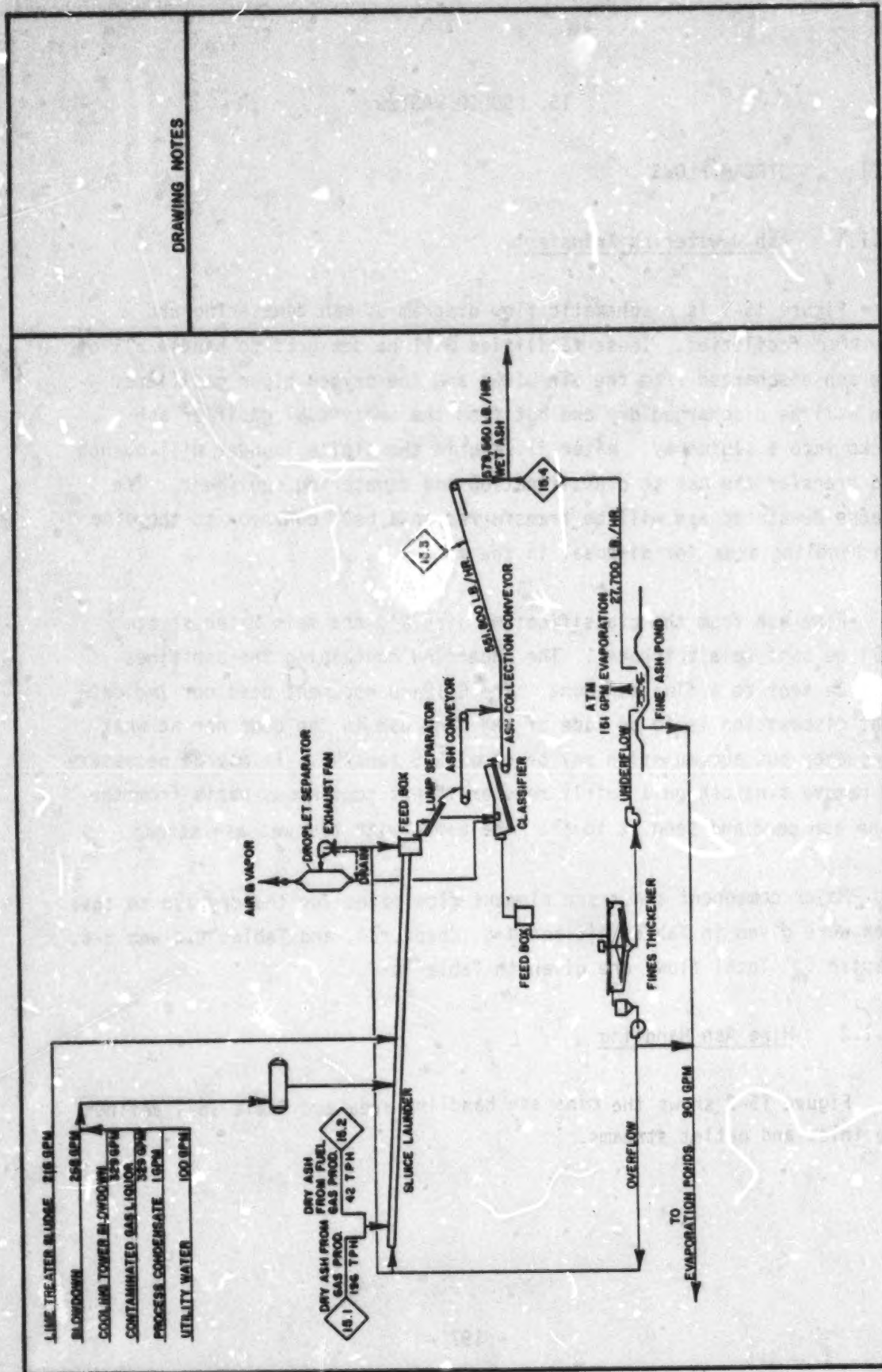
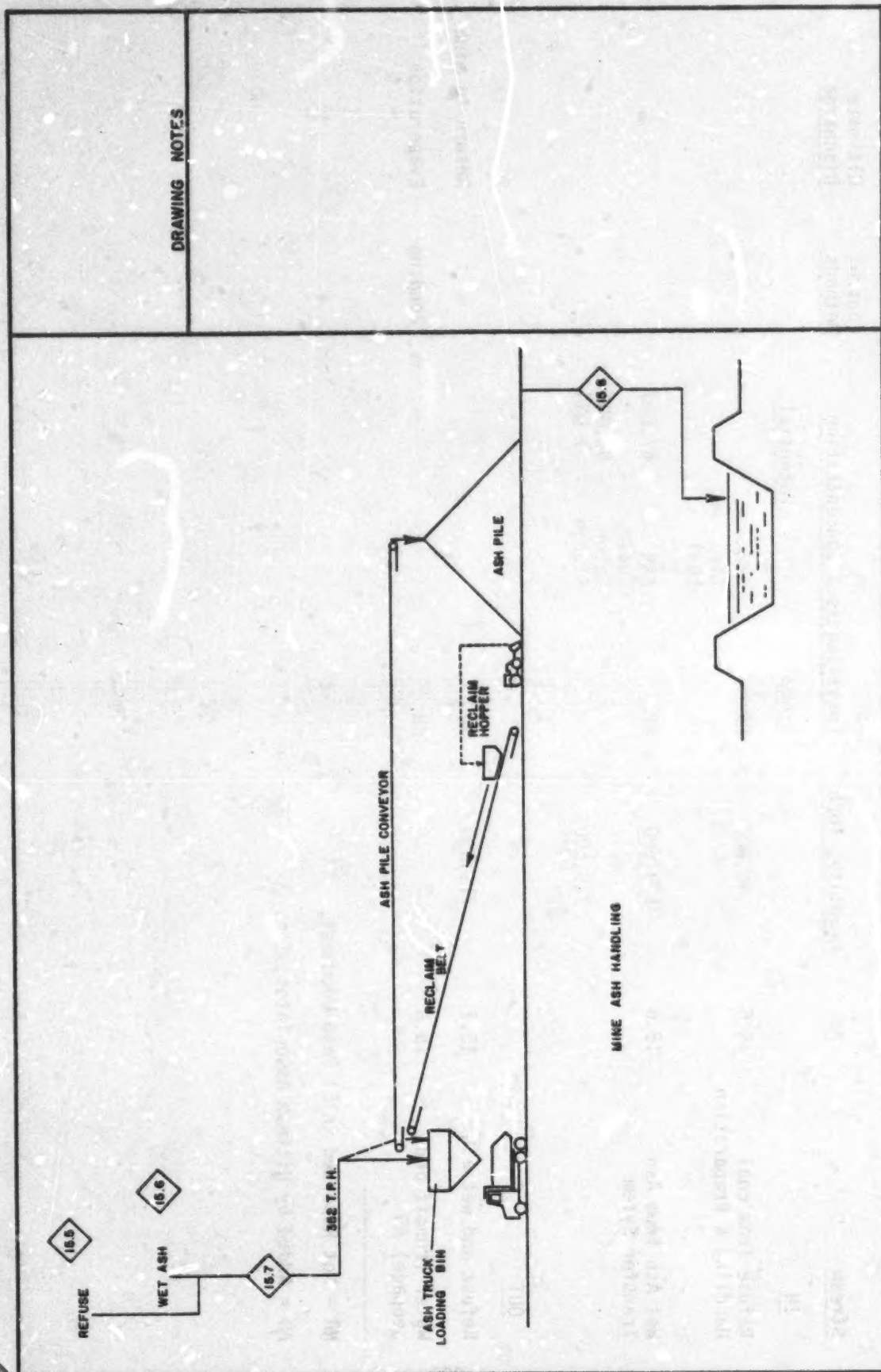


Figure 15-1. FLOW SCHEME FOR THE ASH DEWATERING AND TRANSFER SECTION



DRAWING NOTES

Figure 15-2. FLOW SCHEME FOR THE MINE ASH HANDLING SECTION

Table 15-1. MINE ASH HANDLING

<u>Stream</u>	<u>No.</u>	<u>Quantity, lb/hr</u>	<u>Constituents & Concentration</u>	<u>Control Methods</u>	<u>Ultimate Discharge</u>
<u>IN</u>			<u>Known</u> <u>Potential</u>		
Refuse from coal Handling & Preparation	15.5	140,000	NR Stone - Dirt - Coal -		
Wet Ash from Ash Transfer Sytem	15.6	<u>579,500</u>	NR Ash - 47,600 Coal - Water - 96,000 Sludge - 7,500		
<u>OUT</u>					
Refuse and wet ash	15.7	719,500	NR		Return to mine
Water (runoff and seepage) AD	15.8		NR	Ponding	Evaporation

NR = Not Reported in El Paso Document.

AD = Added by Hittman Associates, Inc.

Inlet Streams. Facilities in this area are designated to receive the wet ash, 572,000 lb/hr, from ash dewatering and transfer, and the refuse, 140,000 lb/hr from coal fines cleaning. These materials are transported by belt conveyors. The wet ash and refuse will discharge from the belt conveyors either into the ash truck loading bin or be transferred by another conveyor to the ash pile for intermediate storage. Wet ash and refuse will be received on a continuous basis in the area.

Outlet Streams. Table 15-2 lists the component and trace element analyses of the dry ash. The wet ash and refuse will be hauled by truck to the mine disposal area on a 10 shift per week schedule. The reclaim conveyor will transfer ash and refuse from the pile to the truck loading bin.

15.2 POTENTIAL EFFLUENTS

15.2.1 Major Pollutants

There may be particulate emissions produced where the hot (200°F+) ash enters the sluice launder. If a closed transfer system is used this will be negligible.

The major solids effluent of course is that contained in the wet ash, whose composition and quantity is given in Table 15-2.

15.2.2 Trace Constituents

Ash Dewatering and Transfer. Trace constituents contained in the dry ash streams entering this area are shown in Table 15-2. Most of these constituents will probably leave this area in the wet ash stream.

Table 15-2. COMPONENT ANALYSIS OF DRY ASH

Coal:	lb/hr	wt. %
carbon	18,186	3.8
hydrogen	1,330	0.28
nitrogen	315	0.066
sulfur	255	0.053
oxygen	3,753	0.785

Ash (Dry Basis):

SiO ₂	281,003	58.953
Al ₂ O ₃	113,308	23.7
Fe ₂ O ₃	22,664	4.7
CaO	17,676	3.7
MgO	4,079	0.85
K ₂ O	3,625	0.76
Na ₂ O	6,798	1.4
TiO ₂	4,079	0.85

Trace Elements:

Sb	0.910	1.9×10^{-4}
As	1.226	2.56×10^{-4}
B	209.490	4.0×10^{-2}
Br	2.960	6.19×10^{-4}
Cd	0.317	6.6×10^{-5}
Cr	663.080	1.38×10^{-1}
Pb	5.680	1.2×10^{-3}
Hg	0.232	4.85×10^{-5}
Ni	45.334	9.5×10^{-3}
Zn	40.990	8.6×10^{-3}

Mine Ash Handling. Potential trace constituents in the ash and in water that may separate from the wet ash include, Sb, As, B, Br, Cd, F, Pb, Hg, Ni, and Zn.

15.3 CONTROL METHODS

15.3.1 Proven Methods

Ash Dewatering and Transfer. No control methods are indicated in the El Paso document for solid effluent controls except for ponding of the underflow from the fines thickener. However, as stated above, the estimated rate of accumulation of fines is some 25,200 lb/hr.

Mine Ash Handling. No planned pollution control methods are described in the El Paso document. It merely states that ash will be transported by truck to the mine disposal area.

15.3.2 Potential Methods

Ash Dewatering and Transfer. Solids collected in the fine ash pond could probably be sent to the mine ash handling area via the wet ash conveyor.

Mine Ash Handling. Some steps that might be taken are:

- provide drainage troughs to collect water that separates from the wet ash being transported on conveyors.
- put the stored wet ash in lined areas (pits depressions) and collect runoff (from both precipitation and seepage).
- treat the wastewaters from the above two steps.

15.4 PROCESS MODIFICATIONS

15.4.1 Ash Dewatering and Transfer

Provide for fine ash transfer from the fine ash pond to the wet ash conveyor.

15.4.2 Mine Ash Handling

Provide for ash storage silos instead of the ash pile, which will eliminate any runoff from the ash pile and will also prevent any carryover of ash to the atmosphere by wind. However, the silos can be expensive and require an economic evaluation.

16. STEAM AND POWER GENERATION

The steam and power generation section is responsible for the generation of electricity, steam and motive power for use in the other processing areas of the plant. Included in the steam and power generation section are the operations of fuel gas cooling, treating and combustion.

16.1 STREAM FLOWS

The process flow scheme and the material balance for the steam and power generation section for the coal gasification plant are shown in Figures 16-1 and Table 16-1, respectively. Raw fuel gas from the fuel gas production section is first cooled in a two-stage cooling operation (air followed by cooling water). The condensate or oily gas liquor produced as a result of this cooling operation is sent to the plant by-product recovery section for recovery of tars, tar oils, phenols and ammonia. Also, a slipstream of the cooled fuel gas is sent to the fuel gas production section for use as coal lock pressurizing gas.

The main portion of the cooled fuel gas stream is directed to the fuel gas treating area where it is contacted countercurrently with regenerated Stretford solution from the by-product recovery section. The Stretford solution, after removing the bulk of the fuel gas H_2S content, is recycled to the by-product recovery section. Section 12 gives a detailed description of the operation of the Stretford process. The resulting desulfurized fuel gas is split into two streams, one going to the methanation section while the larger portion is directed to the gas turbines.

The power generation facilities include fuel gas-fired gas turbines which drive compressors and electrical generators, while the steam generation facilities consist of waste heat boilers associated with the gas turbines and a fuel gas-fired steam superheater. The combustion gases from these units are discharged directly to the atmosphere. Demineralized water from the plant raw water treatment section is used as boiler feed water, while the blowdown from the boilers is used as plant cooling system makeup water.

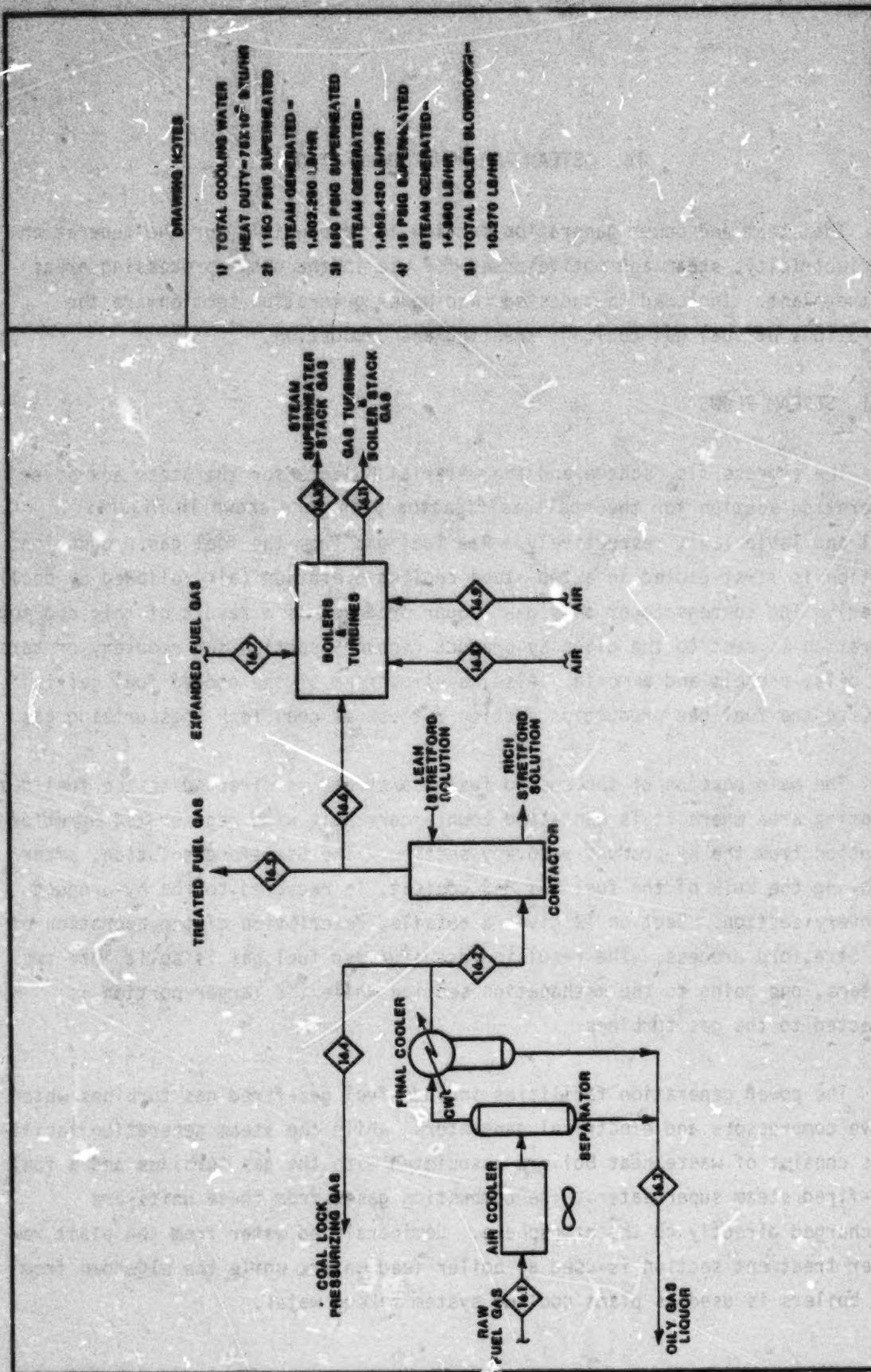


Figure 16-1. FLOW SCHEME FOR THE STEAM AND POWER GENERATION SECTION

Table 16-1. MATERIAL BALANCE FOR THE STEAM AND POWER GENERATION SECTION

Stream Number	16.1	16.2	16.3	16.4	16.5	16.6	16.7	16.8	16.9	16.10	16.11
Stream Description	Raw Fuel Gas	Cooled Fuel Gas	Oily Gas Liquor	Coal Lock Pressurizing Gas	Treated Fuel Gas to Product Compression	Fuel Gas to Boilers and Superheaters	Fuel Gas to Gas Turbines	Air to Steam Superheaters	Air to Gas Turbines and Boilers	Steam Superheater Stack Gas	Gas Turbines and Boilers Stack Gas
Units, lb/hr											
Molecular wt.											
CO ₂	232,981	242,583	9,317	1,081	35,006	28,712	287,577	-	-	76,507	532,946
CO	182,487	181,670	6	809	26,218	31,504	135,652	-	-	-	-
CH ₄	30,432	30,291	6	135	6,372	3,266	25,919	-	-	-	-
H ₂ S	2,951	2,942	-	13	25	20	146	-	-	-	-
C ₂ H ₆	2,618	2,606	-	12	378	210	2,228	-	-	-	-
C ₃ H ₈	4,261	4,242	-	19	612	392	3,620	-	-	-	-
C ₄ H ₁₀	402,901	401,113	-	1,788	57,883	47,476	343,230	195,000	6,455,633	243,271	4,790,717
H ₂ O	17,510	17,425	4	77	2,510	2,062	16,915	-	-	29,935	341,186
N ₂	150,431	1,674	156,950	7	239	196	1,435	1,293	36,247	-	-
H ₂	4,308	4,289	-	19	623	311	3,606	-	-	-	-
Naphtha	6,022	-	6,022	-	-	-	-	-	-	-	-
Tar Oil	132,196	-	-	-	-	-	-	-	-	-	-
Phenol	1,568	-	1,568	-	-	-	-	-	-	-	-
SO ₂	2,771	-	1,568	-	-	-	-	-	-	-	-
SO ₃	-	-	3,771	-	-	-	-	-	-	-	-
O ₂	-	-	-	-	-	-	-	-	-	-	-
Total, lb/hr	1,072,404	888,835	179,509	3,960	127,866	104,879	758,198	256,663	1,348,763	361,333	6,598,837
Temperature, °F	280	90	90	90	90	-100	90	60	60	260	300
Pressure, psia	240	250	250	250	250	14.7	250	14.7	14.7	14.7	14.7

NOTE: All streams are gas phase except for the "Oily Gas Liquor" stream which is a liquid.

16.2 POTENTIAL EFFLUENTS

The effluent streams from the steam and power generation section include:

- Oily Gas Liquor
- Coal Lock Pressurizing Gas
- Treated Fuel Gas
- Combustion Gases
- Boiler Blowdown
- Fugitive Emissions

The following sections discuss the pollutants contained in the above effluents. The major pollutants are addressed in Section 16.2.1, while Section 16.2.2 discusses the trace constituents. For the purpose of this study, trace constituents are assumed to be those components originally entering the steam and power generation section in trace quantities.

16.2.1 Major Pollutants

Before the presence of pollutants in effluent streams from the steam and power generation section can be addressed, the pollutants present in the inlet streams to the area must be identified. The three inlet streams to this area are the raw fuel gas and the two air streams. While the latter two streams are essentially pollution free, the raw fuel gas stream contains the following major pollutants:

- H_2S , COS and other organic sulfur compounds
- Naphthas

- Tar Oil

- Tar

- Phenols

- NH₃

The other major components of the raw fuel gas stream are considered to be desirable constituents. The following sections discuss what is known about the fate of these major pollutants in the steam and power generation section.

Oily Gas Liquor. The condensate streams formed as the raw fuel gas is cooled are combined and directed to the by-product recovery section. This condensate, or oily gas liquor, contains essentially all of the tars, tar oils, phenols and ammonia originally present in the raw fuel gas stream entering the steam and power generation section. Some CO₂, CO, CH₄, and H₂ are also present in the oily gas liquor. The percent composition of this liquid stream is shown below.

<u>Component</u>	<u>Wt %</u>	<u>Component</u>	<u>Wt %</u>
H ₂ O	87.4	NH ₃	2.1
CO ₂	5.2	Tar Oil	3.3
H ₂	<0.1	Tar	0.9
CH ₄	<0.1	Phenol	1.1
CO	<0.1		

Tables 8-2 through 8-4 in Chapter 8 give further details on the compounds that constitute the tars, tar oils and phenols.

Coal Lock Pressurizing Gas. The temperature of the gas leaving the final fuel gas cooler is estimated to be approximately 90°F. At this temperature, only negligible amounts of tars, tar oils, phenols and ammonia remain in the gas phase. Therefore, since the coal lock pressurizing gas is withdrawn from

this stream, it too has negligible quantities of these pollutants. However, this stream does contain H_2S , COS and other organic sulfur compounds since these compounds are still present in the fuel gas stream. The percentage composition of the coal lock pressurizing gas is shown below.

<u>Component</u>	<u>Vol %</u>	<u>Component</u>	<u>Vol %</u>
CO_2	14.8	C_2H_6	0.4
CO	17.4	N_2	38.5
CH_4	5.1	H_2	23.0
$H_2S + COS$	0.2	H_2O	0.2
C_2H_4	0.3	Naphtha	0.1

Treated Fuel Gas. A portion of the treated fuel gas is directed to the methanation section for use in a gas expander that drives the product gas compressors. The fuel gas contains some naphtha and a very small quantity of sulfur compounds. Essentially all of the tars, tar oils, phenols and ammonia, and a large majority of the sulfur compounds originally present in the raw fuel gas are removed in upstream processing operations. The composition of this treated gas stream is shown below.

<u>Component</u>	<u>Vol %</u>	<u>Component</u>	<u>Vol %</u>
CO_2	14.8	C_2H_6	0.4
CO	17.4	N_2	38.5
CH_4	5.1	H_2	23.2
$H_2S + COS$	<0.1	H_2O	0.2
C_2H_4	0.3	Naphtha	0.1

Stack Gases. The steam superheater, gas turbine and boiler stack gases contain combustion products such as SO_2 , NO_x , H_2O , CO_2 , CO, hydrocarbons and air. Because the fuel to these combustion operations is treated fuel gas, the resulting stack gases contain negligible amounts of particulate matter. The use of excess air tends to minimize the amounts of CO and hydrocarbons in the stack gas. The anticipated compositions of the stack gases are shown in Table 16-2.

Table 16-2. COMPOSITION OF STACK GASES

Component	Steam Superheater Vol %	Gas Turbines + Boilers Vol %
CO ₂	14.0	5.5
H ₂ O	13.3	5.9
O ₂	3.0	13.7
SO ₂	48 ppmv	20 ppmv
NO _x	24 ppmv	46 ppmv
N ₂	69.7	74.9

Boiler Blowdown. The boilers in the steam and power generation section use demineralized water for boiler feed water. This inlet water stream is essentially free of all dissolved solids, except for small amounts of silicates. To prevent scaling of the boiler tubes, a portion of the boiler water is removed as blowdown. Since the boilers are operated at approximately 100 cycles of concentration, the blowdown stream contains 100 times the inlet water concentration of dissolved solids. However, because of the high purity of the inlet stream, the blowdown is still relatively free of dissolved solids and is sent to the plant cooling system for use as makeup water.

Fugitive Emissions. Fugitive emissions from the steam and power generation section arise from leaks around valves, flanges, connections, etc. No estimate of the quantity of fugitive emissions can be made, although high pressures like those found in this section tend to increase the severity of the fugitive emission problem. Any of the materials present in the process streams found in this section could be released as a fugitive emission.

16.2.2 Trace Constituents

The inlet gases to the steam and power generation section may contain any of the trace elements present in the coal feed to the gasification section

(see Section 4). Prediction of the fate of these trace elements is complicated by a lack of knowledge regarding the chemical form in which they exist, i.e., as oxides, hydrides, sulfides, etc. It is anticipated that as the gases are cooled, certain trace elements will be removed from the gas phase. Some of the more volatile trace elements such as mercury, bromine, chlorine, fluorine, selenium and tellurium may be retained in the gas phase. Less volatile trace elements might have a higher likelihood of being found in the condensates produced during the cooling operations. Exact quantification of the trace element distribution in the effluent streams from the gas cooling section cannot be made at this time, however. The trace elements found in the condensate streams from one commercial Lurgi coal gasification facility were given in Table 7-2. Trace element balances for the gas liquor streams were calculated for the El Paso feed coal composition and given in Tables 4-9, 4-10, 4-11, 5-7, and 5-8.

Trace elements may also be present in the combustion gases leaving the steam and power generation section. For the same reasons mentioned in the previous paragraph, no definitive statement can be made as to which trace elements, if any, may be present in these effluents.

It is anticipated that the combustion gases will contain unburned hydrocarbons and carbon monoxide. However, since the data on the combustion characteristics of the fuel gas are limited, no estimates are given for the quantities of these pollutants.

16.3 CONTROL METHODS

16.3.1 Proven Methods

Oily Gas Liquor. The contaminated condensates generated during the cooling operations in this section are sent to the by-product recovery section for removal and recovery of tars, tar oils, phenols, ammonia and dissolved gases. These operations are discussed in detail in Section 11.

Coal Lock Pressurizing Gas. A slipstream from the cooled fuel gas stream is used to pressurize the coal locks in the gas production area. Since this stream contains sulfur compounds and naphtha, provisions must be made in the fuel gas production area to contain and recycle essentially all of the lock gas. Section 6 discusses in detail the operation of the coal locks and the emissions resulting from their use.

Treated Fuel Gas. A portion of the treated fuel gas stream is sent to the methanation section wherein the energy content of the fuel gas associated with its high pressure is utilized to drive the product gas compressors. The operation of these compressors is discussed in Section 10.

Combustion Gases. The gases resulting from the combustion of fuel gas in the steam and power generation section contain only very minimal amounts of pollutants since sulfur compounds, ammonia, and heavy hydrocarbons are removed from the fuel gas prior to combustion. The combustion gases are discharged directly to the atmosphere.

Boiler Blowdown. The blowdown streams from the boilers are collected and used as makeup water to the plant cooling system. The dissolved solids content of these blowdown streams is relatively low and does not represent an environmental problem. No other pollutants are anticipated to be present in the blowdown streams.

Fugitive Emissions. Fugitive air emissions are inevitable in any process which contains fittings, valves, flanges, etc. The high pressures encountered in the steam and power generation section tend to increase the likelihood of having fugitive emissions. While fugitive emissions cannot be completely eliminated, the use of best-available technology such as mechanical seals on pumps can help to minimize these emissions. Good maintenance practices also help to minimize fugitive emissions.

16.3.2 Potential Methods

The control methods just discussed in the previous section provide adequate control of the contaminants present in the effluents from the steam

and power generation section. As is evident by this discussion, many of the control methods are actually other processing areas of the plant. Because of this consideration, effluent control alternatives are not discussed in detail here, but reference is made to the process modification sections of other appropriate chapters of this report for detailed examination of alternative controls.

16.4 PROCESS MODIFICATIONS

16.4.1 Fuel Gas Cooling

Potential process modifications to the fuel gas cooling area of the steam and power generation section are constrained by the requirements of downstream processing units. It is thus difficult to envision a process modification in the cooling area that would simultaneously fulfill the process requirements and have a significant impact upon the process effluents.

16.4.2 Fuel Gas Treating

The fuel gas treating area of the steam and power generation section is designed to remove sulfur compounds from the cooled fuel gas. There are many commercial processes capable of removing essentially 100% of the sulfur compounds from gas streams. Some of these systems are listed in Table 16-3. In conjunction with the discussion in Section 9.4, the Rectisol II process is addressed here as a potential process modification to the fuel gas treating area.

The operation of the Rectisol II process is based on the different solubilities of various gases in cold methanol. The solubility of C_3+ hydrocarbons, H_2S , COS , organic sulfur compounds and CO_2 in methanol is significantly greater than the solubility of the valuable gaseous constituents such as CO , H_2 , CH_4 , C_2H_4 and C_2H_6 (see Figure 9-1). Thus, the Rectisol II process is capable of absorbing contaminants from a gas stream while removing only minor portions of the desirable gases.

Table 16-3. COMMERCIALY AVAILABLE ACID GAS REMOVAL PROCESSES

Physical Solvent Processes	
Rectisol	Manchester
Purisol	Perox
Estasolvan	
Fluor Solvent	Fixed-Bed Adsorption
Selexol	Haines
	Molecular Sieve
Chemical Solvent	
MEA	Catalytic Conversion
DEA	Holmes-Maxted
MDEA	Carpenter-Evans
DIPA	
DGA	
Glycol - Amine	
Benfield	
Catacarb	
Chemical/Physical Solvent	
Amisol	
Sulfinol	

As indicated in the discussion of the Rectisol II process in Section 9.4, the methanol leaving the second stage of the main absorber is rich in CO_2 but very lean in H_2S , COS and other organic sulfur compounds. By using a portion of this CO_2 -rich methanol stream, the cooled fuel gas can be treated for removal of sulfur compounds, without simultaneously removing CO_2 and the valuable gases. It is undesirable to remove CO_2 since the fuel gas is used in a gas turbine.

Stream Flows. The process flow scheme and the material balance for the portion of the Rectisol II process associated with the fuel gas treating area of the steam and power generation section are given in Figure 16-2 and Table 16-4 respectively. Cold methanol (-50°F) from the gas purification section is split into two streams; one stream is sent to the prewash column while the other stream is sent to the main absorber. In the prewash column, naphtha and water as well as any residual ammonia and heavy hydrocarbons in the cooled fuel gas stream are absorbed. The methanol from this column goes to the prewash flash column where least soluble gases are desorbed by reducing the stream pressure to atmospheric. The prewash flash overhead stream will contain some H_2S , COS and other organic sulfur compounds and is directed to the plant by-product recovery section where the sulfur compounds are converted into and recovered as elemental sulfur. The flashed methanol from the prewash flash is returned to the gas purification section for further treatment.

The overhead from the prewash column is sent to the main absorber where it is contacted with additional cold methanol for removal of H_2S , COS and other organic sulfur compounds. Depending on the operation parameters of this absorber, essentially all of the sulfur compounds can be removed. The desulfurized fuel gas exits the top of the absorber while the CO_2 - and H_2S -rich methanol from the bottom of the absorber is returned to the gas purification section for regeneration.

Process Effluents. The only true effluent from the above described Rectisol II process is the prewash flash overhead stream. As mentioned previously, this stream contains sulfur compounds and is directed to the plant by-product recovery section for treatment. The anticipated composition of this stream is shown below.

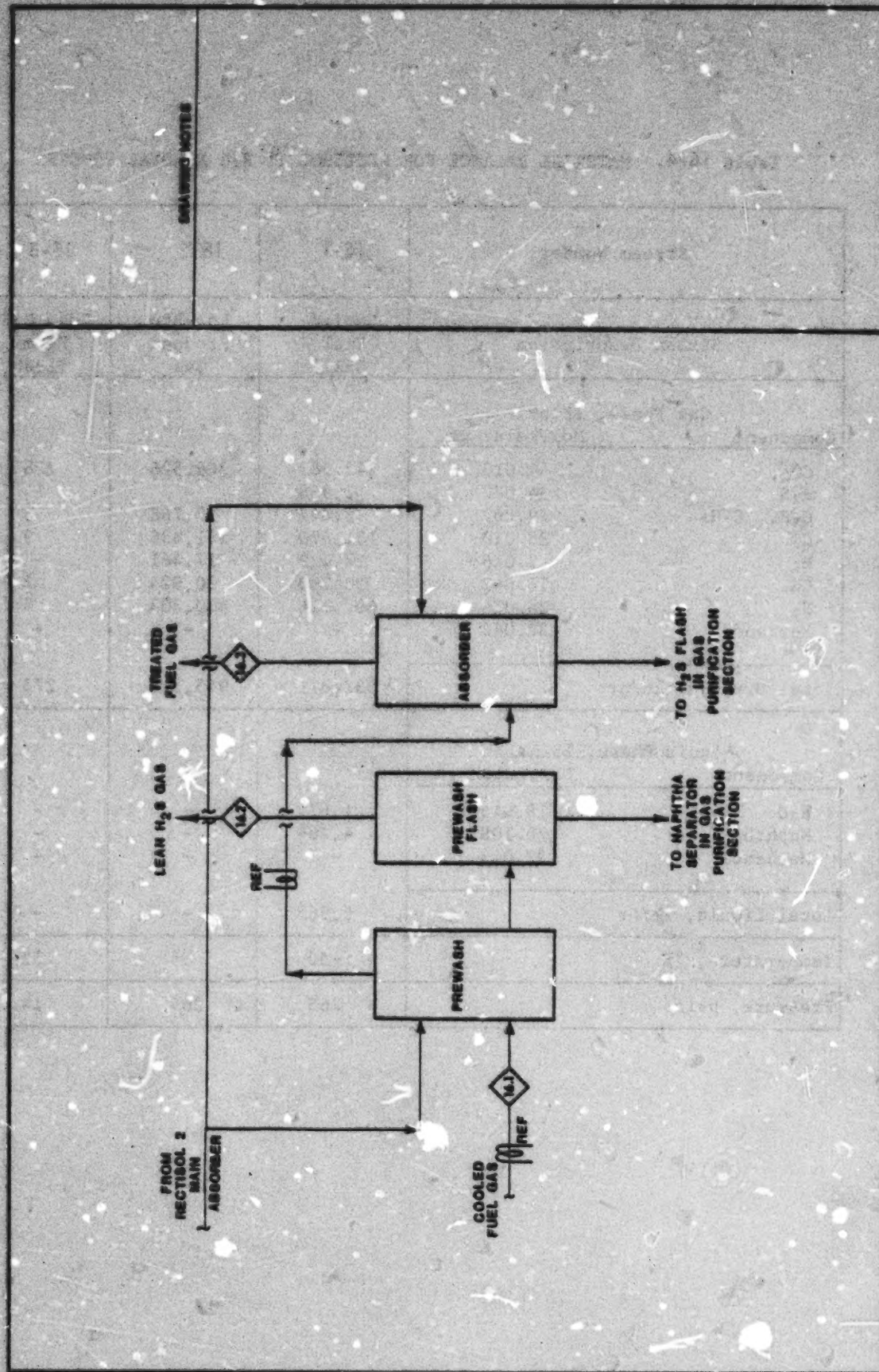


Table 16-4. MATERIAL BALANCE FOR RECTISOL II H₂S REMOVAL PROCESS

Stream Number		16-1	16-2	16-3
Stream Description		Cooled Fuel Gas	Low-Btu Product Gas	Lean H ₂ S From Flash
Gas Phase, lb/hr				
Component	Molecular wt.			
CO ₂	44.010	242,583	306,526	238
H ₂ S	34.082	2,938	-	14
C ₂ H ₄ , C ₂ H ₆	29.262	6,847	7,768	3
CO	28.010	181,670	181,836	9
H ₂	2.016	17,429	17,461	-
CH ₄	16.042	30,290	30,924	3
N ₂	28.016	401,114	400,803	6
Methanol	32.042	-	-	-
Total Dry Gas, lb/hr		882,871	945,318	273
Liquid Phase, lb/hr				
Component	Molecular wt.			
H ₂ O	18.016	1,674	-	-
Naphtha	78.108	4,289	-	-
Methanol	32.042	-	-	-
Total Liquid, lb/hr		5,963	-	-
Temperature, °F		-50	35	32
Pressure, psia		265	265	14.7

<u>Component</u>	<u>Vol %</u>	<u>Component</u>	<u>Vol %</u>
CO ₂	81.4	H ₂	-
H ₂ S	6.2	CH ₄	2.8
C ₂ H ₄ , C ₂ H ₆	1.6	N ₂	3.2
CO	4.8		

The methanol streams exiting the bottom of the prewash flash column and the main absorber are returned to the gas purification section for removal of absorbed constituents.

16.4.3 Fuel Gas Combustion

The fuel gas combustion area of the steam and power generation section is designed to utilize both the pressure and the heating value of the fuel gas to provide steam, electricity and motive power for the gasification plant. The use of alternate process equipment in this area would have only minimal impact on the environmental aspects of the combustion effluents. However, a potentially viable process modification involves the use of fuels other than treated fuel gas.

Since the Lurgi coal gasification process produces by-product tars and tar oils, it may be feasible to use these heavy hydrocarbons to supply all or a portion of the fuel requirements of the plant. Direct burning of coal or coal fines generated in the coal pretreatment operations is also potentially viable alternative.

The main disadvantage to the use of tars, tar oils or coal as a fuel source is the need to treat the resulting combustion gases since all of these fuel sources may contain significant quantities of sulfur. In addition, if coal is used, provisions must be made for controlling the emission of particulate matter. Before any of these alternatives are used, a careful analysis of the economic and environmental considerations of each alternative must be undertaken.

17. OXYGEN PLANT

17.1 STREAM FLOWS

Oxygen requirements are 470,640 lbs/hr or approximately 5600 tons/day. The oxygen is produced by direct separation from air in three identical trains. In each train air flows through a heat exchanger to an air compressor which compresses the air to 85-90 psig. Moisture in the air is condensed and made available for process use. The quantity of condensate water will be highly variable, depending upon the relative humidity of the incoming air. The El Paso design removes approximately 3500 lb/hr of water. After compression, the air enters the cryogenic box and is separated into oxygen and nitrogen by distillation. The oxygen stream will contain approximately 98% oxygen and 2% nitrogen and argon. This stream is compressed to 500 psig and sent to the Lurgi gasifiers. The nitrogen stream contains approximately 429 ppm CO₂, 0.2% H₂O, 0.9% O₂ and 99% N₂⁽⁶⁾. This stream is vented directly to the atmosphere except for perhaps 265 tons/day utilized in the gasification plant⁽³⁾. A schematic flowsheet is given in Figure 17-1. The material balance is given in Table 17-1.

Table 17-1. MATERIAL BALANCE FOR THE OXYGEN PLANT

Stream Component	17.1 lbs/hr	17.2 lbs/hr	17.3 lbs/hr	17.4 lbs/hr	17.5 lbs/hr	17.6 lbs/hr	17.7 lbs/hr	17.8 lbs/hr
N ₂	1,978,854	406,663		1,540,187	21,728			
O ₂	599,008	123,100	406,365	15,336	216			
N ₂ + Ar			10,275					
H ₂ O	16,098	2,586		9,856	139	900,000	3,517	4,000,000
TOTAL	2,593,960	532,349	470,640	1,565,379	22,083	900,000	3,517	4,000,000

Compressors can be driven by steam or by gas turbine. Steam requirements are on the order of 900,000 lb/hr⁽²⁾.

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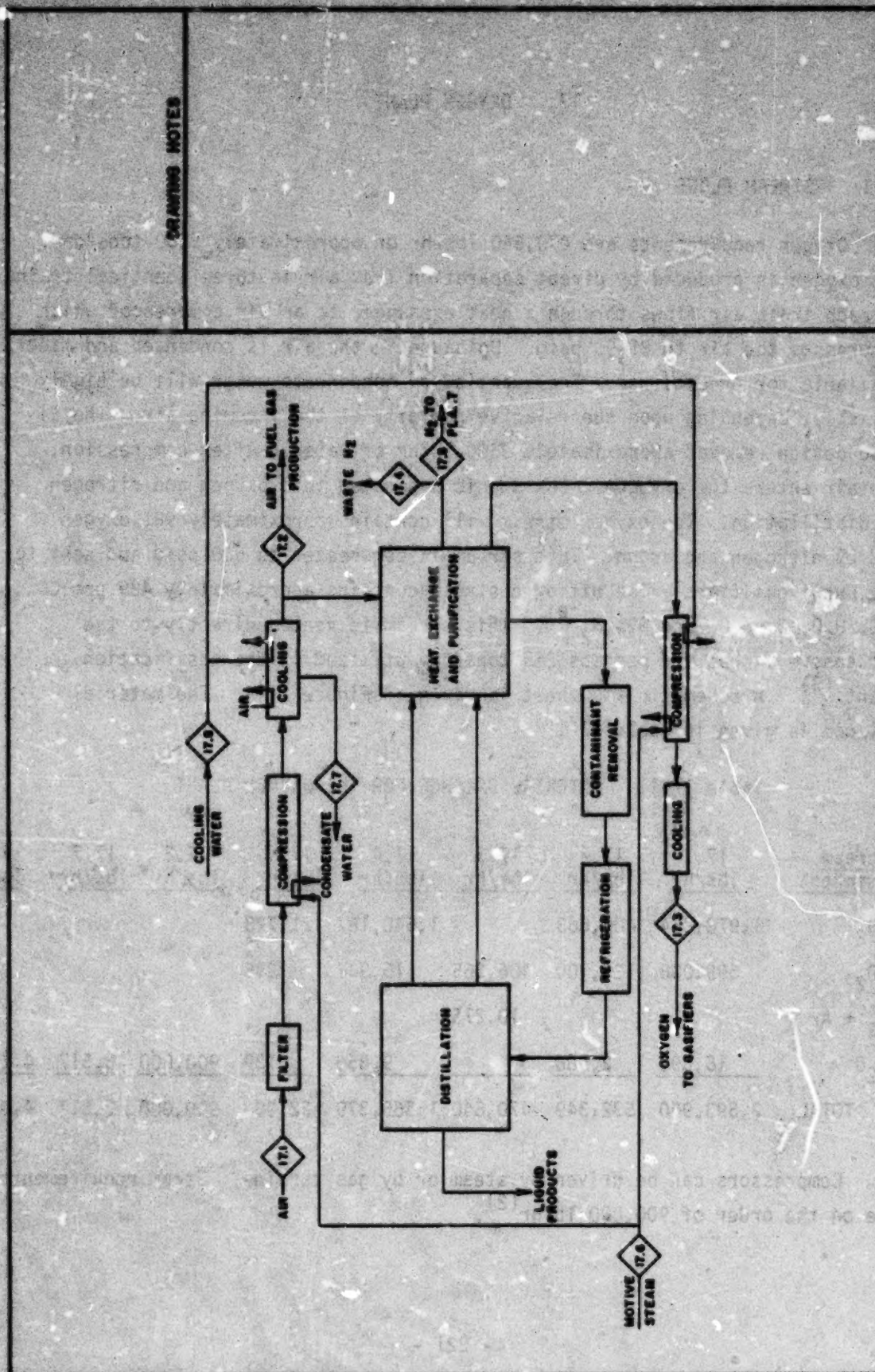


Figure 17-1. FLOW SCHEME FOR THE OXYGEN PLANT

17.2 POTENTIAL EFFLUENTS

No chemical reactions take place in the air separation process and no chemicals are added to the process streams. Therefore there does not appear to be any potential for atmospheric pollution. The nitrogen vent stream merely returns to the atmosphere the major part of the air intake stream without any chemical alteration of the components.

Condensate water removed from the air stream will be supplied to the plant water system as high quality water. Steam condensate will be returned. Thus no environmental pollutants are expected. A cooling water requirement of 8,000 gpm (15°F rise) must be considered when analyzing drift from cooling towers as a pollutant.

In summary, there does not appear to be any significant pollution potential involved with the oxygen production plant itself. Oxygen plant design will indirectly influence overall gasification plant emissions through the choice of power to drive the compressors. Trade-offs can be made between steam turbine, gas turbine and electric drivers. The choice should be made on the basis of overall plant steam and power balances.